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ADVANCED WASTE TREATMENT BY DISTILLATION

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GPO 807-761-1

ADVANCED WASTE TREATMENT BY DISTILLATION

by

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for

The Advanced Waste Treatment Research Program
Basic and Applied Sciences Branch
Robert A. Taft Sanitary Engineering Center

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Public Health Service Publication No. 999-WP-9

ADVANCED WASTE TREATMENT RESEARCH PROGRAM

The Advanced Waste Treatment Research Program of the Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced Waste Treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply problems — problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare ". . . to develop and demonstrate practicable means of treating municipal sewage and other water-borne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use."

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technol-

ogy, one thing is certain — it must be the very lowest science and engineering can achieve. Anything more will impose an inexcusable, perhaps intolerable burden on our country's economic growth and on its ability to compete in tomorrow's world.

W. L. Badger Associates, Inc. was founded by the late Walter L. Badger, Professor of Chemical Engineering at the University of Michigan and an authority on evaporation. The company has been interested for some time in water treatment and in 1955 presented a scheme for sea-water distillation that was used in the million-gallon-per-day demonstration plant at Freeport, Texas.

Joseph H. Neale, author of this report, has had experience in both industrial and municipal waste-water treatment. His first work with Badger was in connection with the Freeport desalination plant.

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ABSTRACT

A desk top study was made of the scaling and corrosion effects to be expected in municipal waste-water distillation. A municipal water re-use cycle was assumed in which sufficient waste-water distillate would be mixed with waste water treated for organic contaminant removal only, to give a mixture suitable for the municipal water supply. The study shows that the concentration of scaling materials is small enough that, in many cases, distillation at a temperature of 400° F should be possible. An economic advantage over sea-water distillation would be expected as a result. Potential corrosion problems exist, but only experimental work will determine the seriousness of these problems.

Continuous boiling experiments were carried out on Ann Arbor sewage to determine the fouling effects of organic contaminants. Distillation of secondary effluent at temperatures up to 250° F should not result in fouling. Data were not obtained above that temperature. Operation with primary effluent does not appear feasible without additional treatment for removal of suspended materials.

ADVANCED WASTE TREATMENT BY DISTILLATION

Introduction

The purposes of this study are to determine scaling and corrosion problems that may be met in distillation of municipal waste for producing potable water for re-use and to evaluate some of the economic aspects of municipal waste-water evaporation. Comparisons with sea-water conversion practices are made where possible.

All conclusions about the effects of inorganic contaminants on corrosion and scaling have been made on the basis of desk studies, but a complete desk study of the effects of organic contaminants proved too extensive. Even if the effects of identified organic contaminants (35% of the total) were determined, we would still not have the over-all picture for organics. Some general conclusions concerning the effects of these materials were drawn from a desk study, but the major determination of organic-fouling effects was made in evaporation tests of Ann Arbor waste water.

In regard to contaminants in municipal waste water, only organic and inorganic materials that would be added by domestic use have been examined. Inorganic contaminants such as iron, chromium, lead, and others that originate as industrial wastes have not been considered. A specific industrial waste in a municipal waste system poses a localized, individual problem and must be examined as such.

With the exception of corrosion and fouling tests on municipal waste water containing a higher-than-average percentage of institutional waste, we have attempted to keep this study general. These two effects are probably common to all municipal systems.

No unit operation or treatment method not directly associated with distillation has been considered in detail. Ultimate disposal of the final waste stream or purification of a bypass stream by adsorption have not been examined and have been considered only insofar as they may be ultimately required.

Conclusions and Recommendations

From this study of scaling potential due to inorganic contaminants in municipal waste water, from experimental fouling tests for organic fouling, and from economic considerations of waste-water renovation by distillation, we conclude:

1. Distillation appears to be practical and economically attractive.

2. A system combining distillation and adsorption could be used to produce potable water for direct re-use to take advantage of cost credits accrued by the elimination of conventional waste-water treatment, water procurement, and water treatment.

3. Pretreatment required for scale control prior to distillation will vary, depending upon the incremental increase of ions through municipal use. Some waste waters will be self-treating, and no pretreatment costs will be incurred.

4. The cost of waste-water renovation by distillation will be less than the cost of sea-water conversion.

5. Distillation should be used in parallel with another, less expensive operation such as adsorption to achieve the lowest cost of product water.

6. Study of the application of distillation to advanced waste treatment should be continued, and a pilot study should be instituted.

Effects of Inorganic Contaminants

Before discussing scaling by inorganic contaminants in the waste-water feed to an evaporator system, we must set two criteria for operation of the distillation plant being considered.

The first criterion is that the plant be operated in parallel with another purification system such as adsorption to reduce the amount of organic contamination while still another operation reduces ammonia to amounts acceptable for potable water. That is, the municipal waste-water feed will be split; part will go to the adsorption plant and the remainder will go to the distillation plant. Both streams will be reblended after processing for delivery to the municipal water system.

The second criterion is that the parallel distillation-adsorption process and municipal usage be operated as a closed system. Waste water processed in the parallel treatment will originate only from municipal use of the product water originating from the purification operations. With these two criteria, we can establish expected analyses of waste-water feeds to distillation plants based on available data and examine the level or degree of potential scaling problems and methods of scale control.

Data on secondary-effluent compositions and tap water analyses have been compiled by the Advanced Waste Treatment Research Program of the U.S. Public Health Service. From these data, 22 cities were selected for which incremental increase of contaminants during water use could be determined. These data were used to evaluate advantages and disadvantages of distillation as applied to advanced waste treatment. Tap water analyses, secondary-effluent analyses, and the corresponding incremental increase data are presented in Tables 1, 2, and 3, respectively. Any generalizations that are made are based on these data, which do not necessarily represent all municipal water and waste-water treatment systems. We would indeed expect to find municipalities where incremental increases of specific ions fall outside the range established by these data.

Table 1. TAP WATER ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MAX	MIN
Organics, ppm:																									
BOD	0	–	–	–	–	–	–	–	–	–	–	–	–	6	0.5	–	–	–	–	–	1	–	2	6	0
COD	0	–	–	–	–	–	–	–	–	–	–	–	–	27	8	42	4	1.4	0	27	–	2	12	42	0
ABS	–	–	–	–	–	–	–	–	–	–	0	0	0.05	0.04	0.02	4.2	0.04	0.02	0.02	0.02	0	0.01	0.37	4.2	0
Cations, ppm:																									
Na^+	27	21	30	97	269	–	–	–	100	33	17	25	–	–	–	–	8	18	17	14	–	10	49	269	8
K^+	–	–	–	–	–	–	–	–	5	4	2	2	–	–	–	–	2	2	2	1.6	–	2	3	5	1.6
NH_4^+	0	–	–	0	0	0	–	0	–	2	0	0	–	–	–	–	0	0	0	0	–	0	0.1	2	0
Ca^{++}	39	28	56	29	17	37	45	–	87	22	58	53	17	–	–	13	20	22	12	108	–	96	42	108	12
Mg^{++}	37	1	17	7	3	Tr	25	–	29	16	7	8	4	–	–	35	5	11	11	30	–	21	16	37	0
Fe^{+++}	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Anions, ppm:																									
Cl^-	13	35	59	53	250	49	150	20	97	32	13	16	15	22	22	518	12	17	9	22	6	16	66	518	6
NO_3^-	9	–	–	–	–	9	22	0	5	2	4	9	–	0.5	0.1	3.0	0.1	6.2	5.3	0.37	–	2.7	5	9	0
NO_2^-	–	–	–	–	–	–	–	–	–	0.3	–	–	–	–	–	0.18	0.03	0.01	0.13	0.31	–	0.03	0.14	0.30	0.01
HCO_3^-	312	35	263	281	347	149	342	268	149	137	176	181	66	–	–	210	27	46	49	379	–	358	198	379	27
CO_3^-	0	10	0	0	0	0	0	–	0	–	0	0	0	–	–	5	1	0	0	0	–	–	0.1	10	0
$SO_4^=$	34	19	21	8	0	58	75	19	291	17	44	47	12	–	–	84	56	79	56	96	–	53	56	291	0
$SiO_3^=$	71	13	30	35	35	–	–	–	11	–	–	–	8	–	–	–	–	–	–	–	–	–	29	71	11
$PO_4^=$ (Total)	0	2	0	0	3	0	0	0	–	2.5	0	0	0	0.5	3.5	3.8	0.04	0.05	0.03	0.02	–	–	8.1	3.8	0
$PO_4^=$ (Ortho)	0	0.5	0	0	1.5	0	0	0	–	–	0	0	0	–	–	3.3	0	0.01	0.01	0	–	–	0.3	3.3	0
Other:																									
Hardness (as $CaCO_3$), ppm	249	74	210	101	55	120	215	220	337	121	174	164	59	–	–	178	71	100	75	150	–	326	158	337	55
Alkalinity (as $CaCO_3$), ppm	255	45	210	230	284	122	280	220	122	112	144	148	54	–	–	180	24	38	40	311	–	294	164	311	24
Total dissolved solids, ppm	364	161	650	504	917	327	500	265	700	–	271	317	100	214	185	1,130	98	177	140	520	155	344	382	917	98
pH	7.8	8.8	7.7	7.8	7.3	7.2	7.8	–	8.0	–	7.7	7.6	8.3	–	–	9.0	8.8	8.2	8.3	7.8	–	7.4	8.0	9.0	7.2

Table 2. SECONDARY – EFFLUENT ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MIN	MAX
Organics, ppm																									
BOD	10	–	18	45	10	–	–	–	–	10	–	–	8	33	9	33	–	–	–	–	18	–	19	9	45
COD	–	–	–	–	–	–	–	–	–	–	–	–	–	135	44	158	163	99	79	49	–	78	101	44	163
ABS	–	–	–	–	–	–	–	–	–	–	6	9	–	2.9	2.4	10.0	10.1	7.2	6.3	4.6	7	9	6.8	2.4	10.1
Cations, ppm																									
Na^+	85	29	–	180	384	–	232	–	200	67	118	99	–	–	–	–	50	68	63	112	–	55	124	29	232
K^+	–	–	–	–	–	–	–	–	20	11	–	–	–	–	–	–	14	9	11	10	–	12	12	9	20
NH_4^+	22	–	–	15	3	5	–	8	44	8	–	–	–	–	–	36	9	21	29	25	–	0	17	0	44
Ca^{++}	96	78	62	45	42	40	58	–	97	33	68	60	–	–	–	–	64	53	54	109	–	97	66	33	109
Mg^{++}	12	16	23	16	17	Tr	26	–	30	17	13	16	–	–	–	–	14	20	22	33	–	22	19	Tr	30
Anions, ppm																									
Cl^-	85	55	121	90	450	165	260	173	197	69	143	79	137	77	64	532	52	67	49	124	90	62	143	52	532
NO_3^-	26	–	–	–	–	–	–	4	2	11	–	–	–	0.04	3.9	6.2	26	22	0.62	26	–	20	12	0.04	26
NO_2^-	–	–	–	–	–	–	–	–	–	2	–	–	–	–	–	0.62	2	0.3	0.26	1.1	–	1.8	1.5	0.26	2
HCO_3^-	303	209	–	420	385	110	298	293	398	200	219	403	146	–	–	327	212	243	314	428	–	409	296	110	428
$CO_3^=$	0	0	0	0	0	0	0	–	0	–	–	–	0	–	–	0	0	0	0	0	–	–	0	0	0
$SO_4^=$	42	57	45	43	20	115	96	70	300	30	75	69	31	–	–	105	95	91	108	111	–	99	84	20	300
$SiO_3^=$	80	30	43	57	49	–	53	25	25	–	–	–	22	–	–	–	–	–	–	–	–	–	43	22	80
$PO_4^=$ (Total)	41	9	37	33	25	50	29	12	–	10	35	43	21	8	5	29	35	19	20	18	–	29	25	5	50
$PO_4^=$ (Ortho)	40	8	34	30	23	32	27	–	–	–	–	–	–	–	–	21.8	33.8	17.9	19	16.9	–	28	25	8	40
Other:																									
Hardness (as $CaCO_3$), ppm	290	259	250	175	175	153	250	230	366	153	224	213	100	–	–	–	218	215	227	411	–	332	235	100	411
Alkalinity (as $CaCO_3$), ppm	248	172	–	344	316	90	244	240	326	164	180	331	120	–	–	268	174	198	257	351	–	335	242	90	351
Total solids, ppm	727	477	844	872	1,362	730	1,041	540	1,065	–	683	566	410	519	410	1,302	472	525	597	648	480	492	703	410	1,362
Suspended solids, ppm	–	–	–	–	–	–	–	–	–	–	–	–	18	–	–	–	–	–	–	–	–	–	–	–	–
pH	6.5	7.1	7.5	7.8	7.3	7.0	8.0	–	7.0	–	–	–	6.9	–	–	7.6	7.5	7.3	7.8	7.8	–	7.4	7.4	6.5	8.0

Table 3. INCREMENTAL INCREASE DATA

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MAX	MIN
Organics, ppm																									
BOD	10	–	–	–	–	–	–	–	–	–	–	–	–	27	8.5	–	–	–	–	–	17	–	16	8.5	27
COD	–	–	–	–	–	–	–	–	–	–	–	–	–	108	36	116	159	98	79	22	–	76	87	22	159
ABS	–	–	–	–	–	–	–	–	–	–	6	9	–	3	2.4	5.8	10	7.2	6.3	4.6	7	9	6.4	2.4	10
Cations, ppm																									
Na^+	58	8	–	83	115	–	–	–	100	34	101	74	–	–	–	–	42	50	46	98	–	45	66	8	101
K^+	–	–	–	–	–	–	–	–	15	7	–	–	–	–	–	–	12	7	9	8	–	10	10	7	15
NH_4^+	22	–	–	15	3	5	–	8	–	6	–	–	–	–	–	36	9	21	29	25	–	0	15	0	36
Ca^{++}	–	50	6	16	25	3	13	–	10	11	10	7	–	–	–	–	44	31	42	1	–	1	18	1	50
Mg^{++}	–	15	6	9	14	Tr	1	–	1	1	6	8	–	–	–	–	9	9	11	3	–	1	6	Tr	15
Anions, ppm																									
Cl^-	72	20	62	37	200	116	110	153	100	37	130	6	122	55	42	14	40	50	40	102	84	46	74	6	200
NO_3^-	17	–	–	–	–	–	–	4	3	9	–	–	–	0.5	3.8	3.2	25.9	15.8	4.7	25.6	–	17.3	10	4.7	25.9
NO_2^-	–	–	–	–	–	–	–	–	–	1.7	–	–	–	–	–	0.4	2	0.3	0.1	0.8	–	1.8	1	0.1	2
HCO_3^-	9	174	–	139	38	39	44	25	249	63	43	222	80	–	–	117	185	197	265	49	–	51	100	44	265
$CO_3^=$	0	10	0	0	0	0	0	–	0	–	–	–	0	–	–	5	1	0	0	0	–	–	1	10	0
$SO_4^=$	8	38	24	35	20	57	21	51	9	13	31	22	19	–	–	21	39	12	52	15	–	46	28	12	57
$SiO_3^=$	9	20	13	22	14	–	–	–	11	–	–	–	14	–	–	–	–	–	–	–	–	–	15	9	22
$PO_4^{\equiv}$ (Total)	41	7	37	33	22	50	29	12	–	7	35	43	21	8	2	25	35	19	20	18	–	–	24	7	50
$PO_4^{\equiv}$ (Ortho)	40	7.5	34	30	21.5	32	27	–	–	–	–	–	–	–	–	18.5	33.8	17.9	19.0	16.9	–	–	25	7.5	40
Other:																									
Hardness (as $CaCO_3$), ppm	41	185	40	74	120	33	35	10	29	32	50	49	41	–	–	–	147	115	152	261	–	6	79	6	261
Alkalinity (as $CaCO_3$), ppm	7	127	–	114	32	32	36	20	204	52	36	183	66	–	–	88	150	160	217	40	–	41	81	36	217
Total solids, ppm	363	316	194	368	445	403	541	275	365	–	412	249	310	305	225	172	374	348	457	128	325	148	320	128	541
pH	1.3	1.7	0.2	0	0	0.2	0.2	–	1.0	–	–	–	1.4	–	–	1.4	1.3	0.9	0.5	0	–	0	0.6	1.7	0

The inorganic contaminants in the feed to a distillation plant will be the total of the incremental ion increase through municipal use plus the ion concentration of the blended distillation and adsorption product waters. On the assumption that there is no change in the inorganic-contaminant concentration, other than ammonia and nitrite, through the adsorption system and only negligible concentrations in the distillate, the analyses of blended product waters after steady state has been established will be a function of incremental ion increase and the fraction of the waste water distilled. If we let f equal the percentage of the total waste water fed to the distillation operation, C_p equal the ion concentration in the blended product water, and C_i equal the increase of the ions during water use, then:

$$C_p = C_i \left(\frac{100}{f} - 1\right) \qquad (1)$$

If C_p is taken as the maximum "acceptable" concentration of a specific ion, then f will be the minimum, and rearrangement of the above equation gives:

$$f = 100 \left(\frac{C_i}{C_p + C_i}\right) \qquad (2)$$

For this report, a set of unofficial maximum "acceptable" concentrations (M"A"C) of inorganic contaminants in the blended product water has been suggested by the Advanced Waste Treatment Research Program of the Public Health Service, and these are shown in Table 4. By application of these M"A"C's to establish the minimum value of f from equation (2) the expected product water analyses for the 22 cities selected have been calculated and are shown in Table 5. The ion concentration of the municipal waste water that will be the feed to the distillation operation and adsorption plant will be the sum of the ions in the product water (Table 5) plus the incremental increase of the ions (Table 3). Table 6 shows these additions and will be used as reference for the examination of scaling by inorganic contaminants and for the economics of operation.

SCALING BY CALCIUM CARBONATE

Calcium carbonate is the least soluble scale expected to be encountered in evaporation of municipal wastes. The bicarbonate in the expected feed (Table 6) will decompose to carbonate and subsequently form calcium carbonate scale.

The commonly accepted methods for controlling this scale are: pH adjustment, degasification under reduced pH conditions for removal of carbon dioxide, ion exchange for calcium removal down to a few ppm, and use of phosphates for preferential precipitation of calcium as calcium phosphate (orthophosphate) or for the sequestering effect of metaphosphate.

Taking the scale control methods in reverse order, we make the following observations.

1. Sequestering of calcium with metaphosphates. This method is applicable to systems operating at relatively low temperatures (below 180°F) because the rate of reversion of metaphosphate increases with increasing temperature. Metaphosphate has been beneficially used in systems operated at higher temperatures, but cannot be used at the anticipated operating temperatures for evaporation of municipal waters (250 to 400° F).

2. Preferential precipitation of calcium as calcium phosphate. Control of calcium carbonate (and calcium sulfate)

Table 4. MAXIMUM "ACCEPTABLE" CONCENTRATION (M"A"C) OF IONIC COMPONENTS IN RENOVATED WASTE WATERS[a]

Ion	M"A"C, ppm
Na^+	110
K^+	50
Ca^{++}	50
Mg^{++}	30
NH_4^+	1
Cl^-	250
NO_3^-	45
NO_2^-	2[b]
$SO_4^=$	250
$SiO_3^=$	50
$PO_4^{\equiv}$	200
Hardness (as $CaCO_3$)	125
Alkalinity (as $CaCO_3$)	250
Total dissolved solids	500

[a] These values were suggested by the Advanced Waste Treatment Research Program for purposes of this report and are not official standards.

[b] NO_2^- is unstable and will convert to NO_3^-. NO_2^- will not, therefore, be limiting.

GPO 807–761–2

Table 5. DISTILLATION – ADSORPTION PRODUCT WATER ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MIN	MAX
Cations, ppm																									
Na^+	80	5	–	110	110	–	–	–	110	110	110	101	–	–	–	–	36	54	38	47	–	110	79	5	110
K^+	–	–	–	–	–	–	–	–	17	23	–	–	–	–	–	–	10	8	7	4	–	26	13	4	23
NH_4^+	31	–	–	1	1	1	–	1	1	1	–	–	–	–	–	1	1	1	1	1	–	1	1	1	1
Ca^{++}	–	34	15	21	24	4	12	–	11	36	11	10	–	–	–	–	37	34	35	0	–	3	19	0	37
Mg^{++}	–	10	15	12	13	–	1	–	1	3	7	11	–	–	–	–	8	10	9	1	–	3	7	1	15
Anions, ppm																									
Cl^-	99	14	160	49	191	144	102	250	110	120	142	86	197	90	93	40	34	54	33	49	129	120	105	14	250
NO_3^-	23	–	–	–	–	–	–	7	0	29	–	–	–	1	8	9	22	17	0	12	–	45	15	0	45
NO_2^-	–	–	–	–	–	–	–	–	–	6	–	–	–	–	–	1	2	0	0	0	–	0	1	0	6
HCO_3^-	0	118	–	184	36	0	0	41	274	204	47	304	129	–	–	305	157	213	218	23	–	135	133	0	305
$CO_3^=$	0	0	0	0	0	0	0	–	0	–	–	–	0	–	–	0	0	0	0	0	–	–	0	0	0
$SO_4^=$	11	26	62	46	19	71	19	83	10	42	34	30	31	–	–	61	33	13	43	7	–	120	40	7	83
$SiO_3^=$	12	14	34	29	13	–	–	–	12	–	–	–	23	–	–	–	–	–	–	–	–	–	20	12	34
$PO_4^{\equiv}$ (Total)	56	5	95	44	21	62	27	20	–	24	38	59	34	12	3	72	30	21	16	9	–	–	34	3	95
Other:																									
Hardness (as $CaCO_3$), ppm	56	125	103	98	115	41	32	16	32	104	54	67	66	–	–	–	125	125	125	125	–	16	79	16	125
Alkalinity (as $CaCO_3$), ppm	0	86	–	151	31	0	0	33	224	168	39	250	106	–	–	250	128	174	178	19	–	107	108	0	250
Total solids, ppm	500	213	500	488	426	500	500	449	401	–	449	341	500	500	500	488	318	378	376	61	500	385	427	61	500
(f)[a]	42.1	59.7	28.0	43.0	51.1	44.6	51.9	37.9	47.6	23.6	47.8	42.2	38.2	37.9	31.0	26.0	54.0	47.9	54.8	67.6	39.4	27.8	42.7	23.6	63.7

[a] (f) means the percent of total waste fed to distillation plant.

Table 6. DISTILLATION FEED WATER ANALYSES [a]

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MAX	MIN
Cations, ppm																									
Na^+	138	13	–	193	225	–	–	–	210	144	211	175	–	–	–	–	78	104	84	145	–	162	145	13	225
K^+	–	–	–	–	–	–	–	–	32	30	–	–	–	–	–	–	22	15	16	12	–	36	27	12	32
NH^+	23	–	–	16	4	6	–	9	–	7	–	–	–	–	–	37	10	22	30	26	–	0	16	0	37
Ca^{++}	–	84	21	37	49	7	25	–	21	47	21	17	–	–	–	–	81	65	77	1	–	4	37	1	84
Mg^{++}	–	25	21	21	27	–	2	–	2	4	13	19	–	–	–	–	17	19	20	4	–	4	14	2	27
Anions, ppm																									
Cl	171	34	222	86	391	260	212	403	210	157	272	92	319	145	135	54	74	104	73	151	213	166	179	54	403
NO_3	40	–	–	–	–	–	–	11	0	38	–	–	–	2	12	12	48	33	0	38	–	62	25	00	48
NO_2	–	–	–	–	–	–	–	–	–	7.7	–	–	–	–	–	1.4	4	0.3	0.1	0.8	–	1.8	2.2	0.1	7.7
HCO_3	0	292	–	323	74	0	0	66	523	267	90	526	209	–	–	422	342	410	483	72	–	184	238	0	526
CO_3	0	0	0	0	0	0	0	–	0	–	–	–	0	–	–	0	0	0	0	0	–	–	0	0	0
SO_4	19	64	86	81	39	128	40	134	19	55	65	52	50	–	–	82	72	25	95	22	–	166	68	19	166
SiO_3	21	34	47	51	27	–	–	–	23	–	–	–	37	–	–	–	–	–	–	–	–	–	34	21	51
PO_4 (Total)	97	12	132	77	43	112	56	32	–	99	73	102	55	20	5	97	65	40	36	27	–	–	62	5	132
Other:																									
Hardness (as $CaCO_3$), ppm	97	310	143	172	235	74	67	26	61	136	104	116	107	–	–	–	272	240	277	386	–	22	158	22	386
Alkalinity (as $CaCO_3$), ppm	0	213	–	265	63	0	0	53	428	220	75	433	172	–	–	338	278	334	395	59	–	148	193	0	433
Total Solids, ppm	863	529	694	856	871	903	1,041	724	766	–	861	590	810	805	725	660	692	726	833	189	825	533	738	189	1,041

[a] Where calculated values were negative, ion concentration is reported as zero.

scale by preferential precipitation of calcium as hydroxyapatite is common in treatment of boiler water and hot phosphate softeners. We think, however, that addition of phosphate is not economically feasible in renovation of wastes where little or no phosphate has been added through use. Cost for phosphate is about 15 to 20 cents per pound of P_2O_5 content. For precipitation as hydroxyapatite each ppm of calcium requires 1.065 ppm P_2O_5. The average calcium content of distillation feed water is 37 ppm (Table 6). The cost for treatment when all the required phosphate must be added in chemical feed would be 5 to 6.5 cents per 1,000 gallons. If calcium precipitated as whitlockite, as would be expected when alkalinity is low, 1.18 ppm P_2O_5 for each ppm Ca would be required at a cost of 5.5 to 7.3 cents per 1,000 gallons. When only a slight phosphate addition is required for calcium precipitation, this method of scale control may be economically attractive. In an open system the addition of make-up water reduces the phosphate: calcium ratio and adds to treatment cost.

3. Ion exchange. Calcium removal through softening by ion exchange can be achieved on either a sodium or hydrogen cycle. Since only the distillation plant feed is softened with ion exchange, the less expensive sodium cycle operation is the more feasible since we are not concerned with an increase in total solids or sodium in the distilled product water. When calcium and magnesium concentrations are small, sulfate concentration is large, and alkalinity is high, then softening by sodium cycle ion exchange may be economically attractive. A serious question arises, however, about the effect of organic contaminants on resin capacity. Organic material may chemically attack the resin or may coat it and act as a barrier to ion exchange. An experimental investigation of this method of scale control is needed.

4. Degasification under reduced pH conditions. This method is being employed for carbonate control in sea-water conversion. Corrosive carbon dioxide from neutralization of carbonate alkalinity is removed along with oxygen. This acid feed-degasification technique is applicable also to pretreatment of waste waters before distillation. In addition to CO_2 and O_2 removal, we would expect removal of volatile organic contaminants. A modification of sea-water degasification by acid feed to a midpoint in the degasification tower could be employed to remove free ammonia prior to acidification.

5. pH adjustment. This method was used in fouling tests

conducted at the Ann Arbor Waste Treatment Plant under this contract. Acid was fed to the waste-feed pump suction with no provisions for removal of gases. This sufficed for test purposes, but may not be recommended for an operating plant inasmuch as corrosive, noncondensable gases must be handled in the distillation system.

Another pretreatment method that has not been used for sea water but may be applicable to waste waters containing high temporary hardness is lime-soda ash softening at temperatures in the 215 to 230° F range. In Table 6, for example, reference city B would have a waste-water feed containing 310 ppm of predominantly temporary hardness. By softening this waste water in a hot-process operation at 220° F, we could expect to reduce the calcium and magnesium to 5 and 1 ppm respectively. The lime and soda ash feed requirements for this operation would be 261 and 138 ppm respectively. With lime costing 0.8 cents per pound and soda ash 2 cents per pound, the chemical feed cost would be about 4 cents per 1,000 gallons. Acid backfeed would be required for carbonate stabilization since the feed would be further heated (~ 350° F) after softening. Since 45 ppm acid would be required to neutralize the alkalinity, acid treatment would cost 0.6 cents per 1,000 gallons with acid priced at 1.5 cents per pound.

For the case in point the maximum permissible operating temperature (based on calcium sulfate solubility product for this distillation plant, and on the assumption that the concentration is the same as the feed at the highest temperature) would be increased from 275° F with pH adjustment to 400° F with lime-soda softening followed by acid backfeed. The 275° F operating temperature is based on $CaSO_4$ solubility product after sulfuric acid feed and will be discussed later.

In consideration of hot lime-soda for pretreatment of a particular waste water, two potentially serious problems must be examined. The first is control of carbonate deposition in equipment used to preheat the water to the desired softening temperature. Methods for controlling scale in sea-water preheaters, such as the sludge-seeding technique, are now under study for the Office of Saline Water and after complete examination in pilot plant operations may be applicable to waste-water treatment. This method of scale control requires thorough pilot studies under waste-water evaporative conditions, since dispersive action expected of organic contaminants may severely alter seed formation and crystal growth.

The second factor to be considered is turbidity of the lime-soda softener effluent. Acid backfeed would be used for stabilization after softening, and the cost of 0.6 cents per 1,000 gallons

assumes an amount of acid just sufficient to neutralize the alkalinity. If carryover or turbidity occurs after softening, excessive acid would be required to react with the softening products, $CaCO_3$ and $Mg(OH)_2$. With organic contaminants such as tannins and lignins in waste water, dispersive action resulting in carbonate and hydroxide carryover from the softener might be expected.

SCALING BY CALCIUM SULFATE

As compared with calcium carbonate-scaling control, calcium sulfate presents a more serious problem because once deposited in heat exchanger tubes it is more difficult to remove. All the scale prevention techniques mentioned under calcium carbonate, with the exception of those requiring pH adjustment, would be applicable to calcium sulfate scale control.

Sequestering of calcium with metaphosphate is more often applied to prevent scaling from temporary hardness than from calcium sulfate deposition because scale is more common from temporary hardness, and, in systems where metaphosphate is applied, the solubility of $CaSO_4$ for the given operating temperature is usually not exceeded. The mechanism for keeping calcium in solution is the same for temporary and permanent hardness. The major deterrent to this technique for $CaSO_4$ scale control is the same as for $CaCO_3$, namely, limited maximum operating temperature.

Preferential precipitation as whitlockite or hydroxyapatite for calcium scale control is equally applicable to carbonates and sulfates. Where phosphates are not added to water through use but must be added as a treating chemical, treatment costs are usually prohibitive.

The sludge-seeding technique for calcium sulfate control has been used for short pilot plant runs in sea-water conversion. More complete studies of this method of scale control will be begun soon and should be closely followed for possible application to waste-water distillation.

A method proposed for scale control in sea-water evaporation is addition of ion exchange resin to the feed stream. Calcium in solution is reduced at the high-temperature end of the distillation plant (where calcium sulfate solubility is minimal), and the resin is regenerated with sodium from the concentrated brine in the low-temperature end (where calcium sulfate solubility increases) and is then recycled. We feel that this method of scale control is not applicable to waste water since the sodium: calcium ratio is much less than for sea water and regeneration through concentration of sodium is negligible.

Hot lime-soda treatment of water high in permanent hardness has the same effect as with water high in temporary hardness, as previously outlined. Two significant differences between lime softening of waste waters of predominantly temporary hardness and of waste waters of predominantly permanent hardness are evident. First, calcium sulfate is much more soluble than calcium carbonate and, in waste water with no alkalinity, as in plants A, F, and G of Table 6, we would expect no scaling of preheaters up to the softening temperature of 220° F. Waste water containing 310 ppm calcium or less stoichiometrically combined with sulfate should offer no difficulty in preheating to softening temperature. Second, the reduction in temporary hardness (alkalinity) will reduce the requirement for less expensive lime, but will increase the consumption of more expensive soda ash. To illustrate: chemical cost for lime-soda treatment without acid backfeed for reference city B was about 4 cents per 1,000 gallons. If we assume no alkalinity, the lime requirement will decrease from 261 to 86.5 ppm and the soda ash feed will increase from 138 to 364 ppm. The lime-soda ash cost will then be 6.6 cents per 1,000 gallons as compared with 4 cents per 1,000 gallons with the temporary hardness.

The maximum permissible operating temperature of sea-water conversion plants is limited by the solubility of $CaSO_4$. The plants can be so designed that greatest sea-water concentration occurs at the lowest temperature (forward feed). This technique can be used in waste-water evaporation. In reference to the $CaSO_4$ solubility product curve of Figure 1, waste water containing a calcium sulfate ion product of 2,000 ppm^2 or less can be evaporated in systems with a maximum operating temperature up to 400° F. Evaporation with concentration at successively lower temperatures must be controlled so that the solubility of calcium sulfate is not exceeded. In systems where sulfuric acid feed is used for pH adjustment, the increase of sulfate ion concentration decreases the maximum permissible operating temperature. The extent of this decrease is shown in Table 7 where the maximum operating temperature based on calcium sulfate solubility product is shown for 12 of the 22 plants with and without acid feed.

SCALING BY MAGNESIUM HYDROXIDE

Magnesium sulfates and chlorides are very soluble in water. Magnesium bicarbonate and carbonate have a solubility of about 35,000 and 100 ppm, respectively, below the atmospheric boiling point of water. Magnesium hydroxide is only slightly soluble in alkaline solutions and exhibits an inverse solubility curve. Car-

bonate and bicarbonate alkalinity break down with increasing temperature to hydroxides and CO_2. This decomposition decreases the solubility of magnesium by increasing the hydroxide ion concentration.

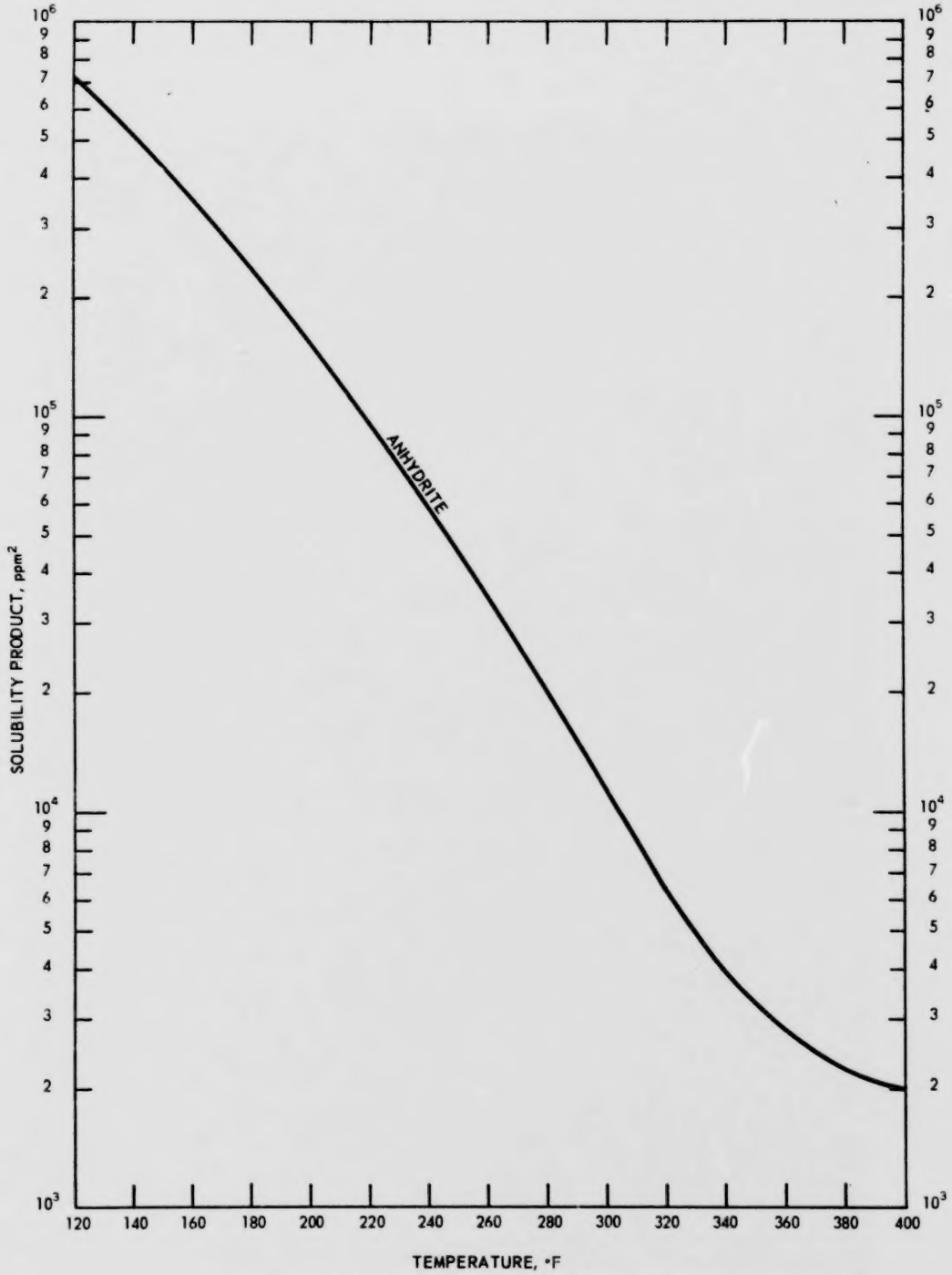

Figure 1. Calcium sulfate solubility product.

The solubility of magnesium hydroxide in water at elevated temperatures is reported in Seidell. [1] Expressing the solubility

Table 7. PRETREATMENT COSTS

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG PLANT
pH adjustment with H_2SO_4																							
acid cost, ¢/1,000 gal	0	2.7	–	3.3	0.8	0	0	0.7	5.4	2.8	0.9	5.4	2.1	–	–	4.2	3.5	4.3	4.9	0.7	–	1.9	2.4
pH adjustment with HCl																							
acid cost, ¢/1,000 gal	0	8.5	–	10.3	2.5	0	0	2.2	16.9	8.8	2.8	16.9	6.6	–	–	13.1	10.9	13.5	15.3	2.2	–	6.0	7.5
Phosphate-silica																							
treatment																							
PO_4 cost, ¢/1,000 gal	–	5.1	0	0	1.5	0	0	–	–	0	0	0	–	–	–	–	2.7	2.7	3.6	0	–	–	1.2
SiO_2 cost, ¢/1,000 gal	–	1.5	0	0	2.3	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	0.8
Total, ¢/1,000 gal	–	6.6	0	0	3.8	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2.0
Hot lime-soda ash																							
treatment																							
Lime cost, ¢/1,000 gal	–	1.7	0.5	1.9	1.0	0	0.1	–	2.4	1.3	0.7	2.8	–	–	–	–	1.9	2.3	2.5	0.4	–	0.9	1.4
Soda ash cost, ¢/1,000 gal	2.5	2.5	–	0.6	3.9	2.0	1.9	0.6	0.6	0.6	1.2	0.6	0.6	–	–	–	0.6	0.6	0.6	6.9	–	0.6	0.6
Acid costs, ¢/1,000 gal	–	0.6	–	0.6	0.6	0.6	0.6	–	0.6	0.6	0.6	0.6	–	–	–	–	0.6	0.6	0.6	0.6	–	0.6	0.6
Total, ¢/1,000 gal	–	4.8	–	3.1	5.5	2.6	2.6	–	3.6	2.5	2.5	4.0	–	–	–	–	3.1	3.5	3.7	7.9	–	2.1	2.6
Maximum operating																							
temperature, °F																							
With H_2SO_4 pH adjustment	–	275	–	295	330	–	–	–	310	295	355	310	–	–	–	–	270	275	260	260	–	400	305
With HCl pH adjustment	–	325	–	355	400	–	–	–	400	370	400	400	–	–	–	–	325	400	400	310	–	400	365
$PO_4^{\equiv}$ - SiO_2 treatment	–	400	–	400	400	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	400	400
Hot lime-soda ash treatment	–	400	–	400	400	–	–	–	400	400	400	400	–	–	–	–	400	400	400	400	–	400	400

product of $Mg(OH)_2$ in ppm^3, a best curve plot of the reported data was made to express the solubility of magnesium in alkaline solutions as a function of temperature and pH. The equations for solubility product and pH of a solution containing magnesium and hydroxide ions are as follows:

$$SP = (Mg)\ (OH)^2 \qquad (3)$$

and

$$pH = 14 - \log \frac{1}{[OH]} \qquad (4)$$

With (Mg) and (OH) expressed as ppm of respective ions and [OH] expressed as gram equivalents per liter, the following expression was developed:

$$\log (Mg) = \log SP + 19.540 - 2\ pH \qquad (5)$$

A plot of magnesium solubility as a function of temperature for various pH values, given in Figure 2, shows that control of magnesium hydroxide scale is accomplished easier by pH control than by magnesium removal such as would be obtained by presoftening of the waste-water feed.

The maximum magnesium concentration in waste-water feed occurred in reference city F of Table 6. A comparison of this magnesium concentration of 27 ppm with sea water, which has about a 1,300 ppm magnesium concentration, shows that magnesium hydroxide scale in waste-water evaporation will be of much less concern than will be calcium carbonate and sulfate scales. When softening with lime and soda ash or when ion exchange resins with pH adjustment are employed for calcium carbonate scale control, control of magnesium hydroxide deposition results.

FOULING BY SUSPENDED INORGANIC CONTAMINANTS

The variety of suspended inorganic contaminants that may possibly be encountered in processing of municipal wastes for reuse is too extensive to warrant a general study, and is mentioned here only because it represents a potential problem in evaporator tube fouling. Suspended clays and the like can readily stick to heat transfer surfaces, bake on to form a hard deposit, and seriously reduce the over-all heat transfer coefficient.

In evaporator tube-fouling studies conducted under this contract, suspended matter fouled the test evaporator tube on the first run when unfiltered primary effluent was used as feed. Subsequent studies were made with unfiltered secondary effluent.

Suspended matter that presents a potential fouling problem may be removed from the feed by mechanical means, or supplementary treatment may be required to keep it in suspension.

FOULING BY INDUSTRIAL WASTES

Although the study of the effect of industrial wastes on tube fouling or corrosion is not within the scope of this report, industrial wastes and their effect on evaporation problems must not be discounted. The individual city accepting a particular waste into its sewage system must be examined in particular.

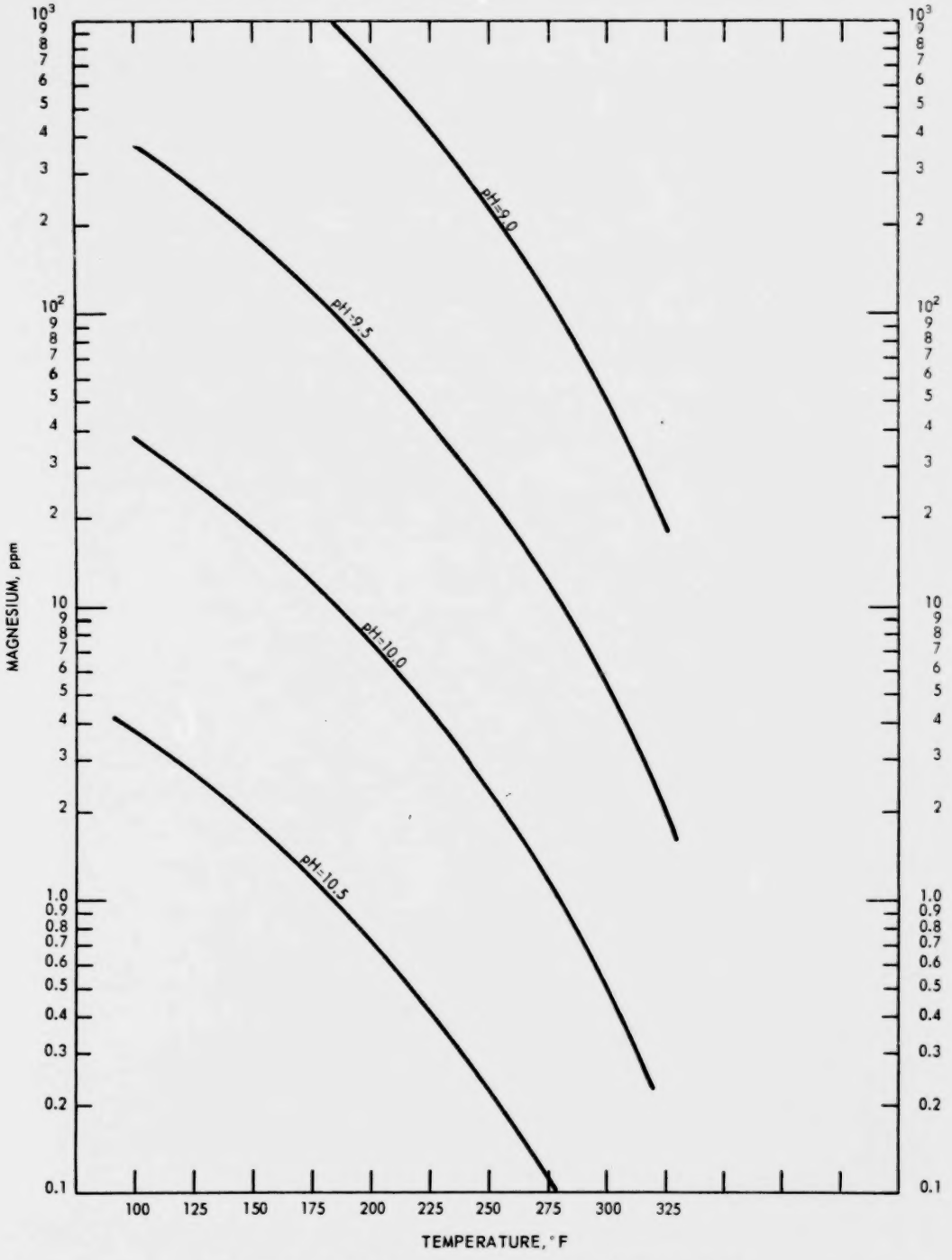

Figure 2. Solubility of magnesium in alkaline solution.

SCALING BY IRON AND SILICA

Inorganic scale resulting from iron or silica should present no problems in evaporation of waste and is discussed here primarily to dispel overconcern about the presence of these materials in waste-water feed.

Silica-containing scales such as acmite, analcite, kaolinite, and natrolite would not be expected to occur during distillation under the operating conditions anticipated for advanced waste treatment. These scales can occur in localized areas of large concentration and high evaporation surface temperatures as may be encountered in boilers. Silica deposits on turbine blades have occurred in central stations where boiler water silica has been excessive. The volatile silica enters the turbine with the steam and coats turbine blades. We should anticipate no such problem with thermocompressors since expected operating temperatures will be far below those occurring in central stations.

Iron is often found in analyses of scales, but is usually present as oxides occluded in the scale and is not chemically combined as scale material. When iron is found chemically combined in scale, the reason is similar to that for silica, namely localized concentration and high skin temperatures.

INTRINSIC TREATMENT

Pretreatment of waste water prior to distillation by addition of phosphate for precipitation of hydroxyapatite or whitlockite with increasing temperature has already been mentioned as a possible treatment method for control of calcium scales. When, however, the phosphate ion must be fed to the wastes, treatment costs become excessive.

Phosphate is added to municipal waste through use as evidenced by the phosphate increment in Table 3. If we assume no phosphate removal through the adsorption process, the average phosphate ion concentration in distillation feed will be 62 ppm. When heated, this phosphate will react with available calcium to precipitate calcium preferentially as whitlockite or hydroxyapatite. Hydroxyapatite will precipitate under alkaline conditions and requires 1.58 pounds of phosphate for each pound of calcium precipitated. Whitlockite will precipitate under reduced pH conditions and requires 1.43 pounds of phosphate for each pound of calcium precipitated. In Table 6 the average concentration of calcium ion is 37 ppm, which gives a PO_4:Ca ratio of 1.68 — more than enough

phosphate for precipitation of all of the calcium. This indicates we should expect the majority of municipalities to have sufficient phosphate already available in the waste water for intrinsic control of calcium scale.

Of the 22 reference cities reported, 13 have data for both calcium and phosphate. Of these, the PO_4:Ca ratio varies from 0.14 to 27 with an average of 5.24. Eight of the 13 cities have enough phosphate to precipitate calcium as whitlockite or hydroxyapatite. This encourages the consideration of distillation for advanced waste treatment since many cities may require no costly chemical feed.

Calcium phosphate normally precipitates as a sludge and, if kept suspended, has no effect on heat transfer coefficient. Under certain conditions calcium phosphate sticks to heat transfer surfaces, which decreases the over-all coefficient. The deposit so formed is not scale-like in that it can be easily removed by a high-velocity water flush or by wet or dry brushing. A common method of controlling this deposit involves the use of dispersives such as tannins and lignins to keep the precipitate suspended. In treatment of municipal waste waters we should fully expect dispersive action owing to the presence of organic contaminants.

The addition of silica to municipal wastes through use and its possible beneficial effect in controlling magnesium scale formation can be compared favorably with phosphate addition and its effect on calcium. A common practice in water conditioning is the addition of silica to hot lime-soda softening systems for magnesium reduction, and the reverse, such as addition of magnesium to water supplies, when silica is a problem. Silicates react with magnesium to precipitate magnesium preferentially as serpentine, a precipitate with much the same characteristics as hydroxyapatite. That is, serpentine is a sludge, and through the natural dispersive action of the organic wastes it should be expected to remain in suspension and not interfere with heat transfer in the evaporator.

For the formation of serpentine, 2.09 pounds of SiO_3 are required for each pound of magnesium in the waste water. In Table 6, there are only five cases for which concentrations of both silicate and magnesium are reported. Of the five, two had sufficient silicate for complete precipitation of magnesium as serpentine. The ratio of the average silicate to the average magnesium (Table 6) is 2.43—more than adequate for serpentine formation.

We would expect to find many municipalities with sufficient silica and phosphate for complete control of scaling and for

avoidance of the extra cost required for chemical conditioning of the feed to the distillation plant.

In evaluation of the economics of pretreatment of waste water, supplemental treatment with phosphate and silica may, in some cases, be more favorable than pH adjustment or lime-soda ash treatment. Chemical costs for pH adjustment of feed, supplemental phosphate-silica feed, and lime-soda ash treatment are shown in Table 7. Sufficient data for comparison of chemical costs are available for only 3 of the 22 plants, but a comparison of these costs with related maximum permissible operating temperatures will illustrate the point.

Acid cost for pH adjustment in plant B will be 2.7 cents per 1,000 gallons and the maximum operating temperature will be 275° F. Treatment by supplemental phosphate-silica feed or by lime-soda ash will increase the maximum permissible operating temperature to 400° F. To achieve the higher temperature, the cost increase for phosphate-silica will be 3.9 cents per 1,000 gallons over pH adjustment. Equipment cost for phosphate-silica feed will be comparable with that of the acid feed system, but the cost of lime-soda ash treatment equipment will add significantly to over-all plant cost.

No requirement for chemical feed is clearly indicated for plant D. The data are, however, based on spot analyses, and supplemental feed may be required at times when intrinsic treatment diminishes. We would expect average chemical cost to be nil, but equipment would be required for standby chemical feed.

The increase in chemical cost of phosphate-silica feed over acid for plant E is 3.0 cents per 1,000 gallons for a corresponding temperature increase from 330 to 400° F. In this case, lime-soda ash treatment would not be competitive, especially when additional capital expenditures are considered. Evaluation of the economy of acid feed versus phosphate-silica treatment for plant E will require closer scrutiny than for plant B since the increase in permissible operating temperature is less.

The above discussion illustrates the need to evaluate each project individually. Even if all the forementioned scale prevention techniques are applicable, the economic evaluation remains, and a general evaluation applicable to all plants is not possible.

Effects of Organic Contaminants

When we remember that only about 35 percent of the organic contaminants in waste water have been identified, it is evident that we can make only general statements about the possible advantageous or disadvantageous effects of organics in distillation of wastes.

We would not expect to encounter scale-like organic deposits in heat exchangers as such. We may have tube fouling that, when related to heat transfer, can be just as detrimental as calcium sulfate, calcium carbonate, or magnesium hydroxide scales. Organic material when deposited on heat transfer surfaces may be porous and bulky, acting as an efficient insulator to hamper heat transfer. This is especially true of insoluble organic contaminants, which may be fed to the distillation system as suspended matter.

The potential tube fouling due to heavy deposits of higher fatty acids and/or polymerization of organic contaminants with increased temperature and pressure is a distinct possibility in waste-water distillation. Deposition of oils and grease, which have an affinity for metal surfaces, can seriously reduce overall heat transfer coefficients, as can deposition of amino acids or coagulation of proteins with subsequent deposition.

Decomposition of organic contaminants to less soluble material is another possibility to be considered, together with the possible salting out of organic contaminants owing to increased concentration of organic and inorganic contaminants in the latter stages of evaporation.

A potential problem, and indeed a most likely one for inclusion here, is bacterial growth, which may be expected to occur in low-temperature ($< 130^{\circ}F$) equipment such as preheaters and the final condenser. Continuous or shock chlorination will most probably be required to control these growths.

From these briefly outlined possibilities one might conclude that any attempt to handle organic wastes in an evaporative system would be doomed to failure. There is, however, a consideration to the contrary: Organic material may actually inhibit tube fouling and otherwise improve operation.

Precipitation of the scale constituents, calcium and magnesium or phosphates and silicates, have been mentioned previously. Although not scales as such, hydroxyapatite and serpentine

could possibly stick to heat exchanger tubes and have the same effect as scale. This condition has occurred many times in boiler water evaporators. When this occurs and is not effectively controlled by pretreatment of feed water, a dispersive is used to keep the phosphates and silicates suspended. We should expect a dispersive action owing to the presence of organic material, especially tannins, lignins, and surface-active agents such as ABS. Hydroxyapatite and serpentine as dispersed material could then be carried through the distillation system with no detrimental effects and finally blown down with the concentrated waste for disposal.

Since there is some evidence that sugars increase the solubility of calcium sulfate in aqueous solutions, sugars in the waste stream may have a beneficial effect in systems where operation is limited by the solubility of calcium sulfate.

Inorganic contaminants originating as industrial waste have been mentioned as presenting a potentially serious problem in waste-water distillation, but this problem is outside the scope of this report. It should be recognized that organic contaminants may react with copper, zinc, etc., and subsequently form salts that can be carried in suspension through the system.

Another possibly beneficial effect of organic contaminants in distillation operations that is a distinct advantage in heat transfer is promotion of dropwise condensation. In the absence of a nonwettable film, vapor, condensing on heat exchanger tubes, completely wets the surface, and a film of condensate remains and acts as a barrier to heat transfer. Volatile organic contaminants, evaporated in a particular effect or stage, will condense with the water vapor in the next lowest temperature effect or stage. If a light organic film is deposited at this point, the surface will be nonwettable, and condensation of water vapor will occur in drops, which will increase the heat transfer coefficient by elimination of the water film.

As stated previously, no conclusions about the effect of organic contaminants on tube fouling could be effectively determined by a desk study since most of the organic contaminants are not identified, and possible reactions of the identified organic contaminants would be pure speculation. On this basis a decision was made to devote more effort to empirical evaluation of organic tube fouling under actual test conditions.

A description of test runs, equipment, and results will be found on pages 26 to 35.

Corrosion

Corrosion attributable to organic material in the first stages in distillation of municipal waste water should be negligible. Even though waste water may contain 400 or 500 ppm of organic contaminants, these are much less ionized than inorganic contaminants, and in concentrations to be expected, will be too weak to set up an effective galvanic cell. A significant difference between corrosion potential and tube-fouling potential as related to concentration of a detrimental material in waste water is that in fouling the action is cumulative, while in corrosion the corrosive material itself does not concentrate in the system. That is, a few ppm of fouling material fed to a system will result in gradual fouling of equipment and an eventual outage. On the other hand, a corrosive constituent must be present in the waste water in concentrations great enough to initiate corrosive action. We do not mean to imply that a low corrosion rate is not a function of contaminant concentration, but concentrations to be expected in waste feeds are not expected to present any problems until final concentration for disposal.

Of much more concern in an assessment of the corrosion potential of organic wastes are their inorganic decomposition products. Sulfides such as hydrogen sulfide, ammonia evolved from decomposition of amines, and carbon dioxide or carbonic acid derived from organic decomposition are considered potential and in some cases opposing corrosion problems.

Aside from materials resulting from organic decomposition, free ammonia and free carbon dioxide can still exist. In addition the latter is evolved in decomposition of bicarbonate and carbonate. The rare case must also be considered wherein free or dissolved oxygen may be encountered in the system.

Copper alloys are common materials of construction for heat exchangers or condensers. Ammonia and sulfide will attack copper, especially at condensing surfaces and, if not oxidized or kept from contact with these surfaces, may preclude the use of copper or copper alloys in distillation equipment. Attacks on ferrous metals by carbonic acid and dissolved oxygen are problems commonly encountered in evaporation, especially in steam boilers and associated condensers.

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The numerous techniques used to control corrosion due to ammonia, hydrogen sulfide, carbonic acid, and dissolved oxygen in aqueous solutions can be grouped into two categories: neutralization and protective film formation. An interesting aspect of the corrosion potential of municipal waste water in advanced waste treatment is that the corrosive inorganic contaminants exist in wastes along with materials that control corrosion by neutralization and protective film formation. The question, however, remains: Are the controls sufficient?

A common method for control of carbon dioxide corrosion in condensate systems is neutralization of carbonic acid with ammonia or neutralizing amines, which are fed to a steam generator or steam line, condensed, and absorbed in condensate on condensing surfaces to neutralize the corrosive carbonic acid. Excess ammonia or neutralizing amines will, however, attack copper alloys. In the absence of other protective devices such as filming amines, a balance between acidic carbon dioxide and basic ammonia must be maintained for corrosion protection.

Hydrogen sulfide will readily attack copper alloys, and can originate in anaerobic digestion of waste in sewerage systems or other retention equipment, or can originate in decomposition of wastes at elevated temperatures. Hydrogen sulfide is readily oxidized to elemental sulfur. Chlorination or air injection in industrial wastes or in sulfide-bearing well waters is a common method for eliminating sulfide corrosion problems. In distillation the above remarks relative to neutralization of carbonic acid with ammonia are equally applicable to hydrogen sulfide.

A quick review of the common causes and cures of corrosion as previously outlined demonstrates that we do have counteracting inorganic contaminants in waste water. The ideal situation would be one in which a perfect balance is achieved: Sufficient ammonia to neutralize all the carbon dioxide and sufficient oxygen to oxidize sulfide, or an ammonia-sulfide balance, or all three.

On first inspection it may appear that all that is necessary to evaluate the corrosion potential of a particular waste water is a chemical analysis of the above-mentioned constituents. This of course is the first step, but equally important is the distribution of corrosive inorganic contaminants in the evaporation system with release of free inorganic and breakdown of organic contaminants. To illustrate, a waste water may have a perfect total ammonia-carbon dioxide balance, but evolution of these two constituents in successive stages of evaporation must be stoichiometric for successful neutralization. One extreme case may be a situation wherein all the carbon dioxide is released in the first stage of evap-

oration and ammonia released from amines in the later stages. Carbon dioxide corrosion in first-stage condensate and ammonia attack on copper in the later stages would result.

Of importance equal to a stoichiometric balance of corrosive inorganic contaminants is the presence of filming amines in the waste-water feed for intrinsic corrosion control. Filming amines are used extensively in condensate systems to control corrosion due to oxygen or carbon dioxide attack. They are added to steam generators or injected into steam lines where they volatilize and recondense on condensing surfaces. The amines have an affinity for metal and lay down a molecularly thin protective film. The film insulates the metal and keeps the corrosive oxygen or carbonic acid from coming in contact with the metal. We should fully expect similar volatilization and condensation of amines in waste-water distillation. There is a question of distribution of filming amines in the evaporation system, but it is not as serious as the distribution of inorganic contaminants or neutralizing amines. For protection with filming amines, it is necessary only to have a few ppm volatilize in each stage. The rate of volatilization for corrosion protection is independent of the corrosive constituent.

A desk study of corrosion problems associated with waste-water distillation leads to the conclusions that many forces will interact and that experimental corrosion studies must be made with distillation pilot plant operations to define these problems further and solve them.

Tube-Fouling Tests

Because of the complexity of a desk study to analyze the fouling potential of organic material in distillation operations, it was decided that tube-fouling tests using waste-water feed from the Ann Arbor Sewage Treatment Plant would be conducted. The basic equipment used in these tests consisted of a jacketed evaporating tube, separator, waste-water feed pump, and boiler. The evaporator tube was a 1-inch, 16 BWG, type 316, stainless steel tube with an effective heat transfer length of 14 feet. The tube jacket was a 1-3/4-inch, 14 BWG, carbon steel tube welded to the 1-inch evaporator tube. No provisions were made for removing the evaporator tube from the jacket for inspection or change

in materials of construction. Type 316 stainless steel was chosen for the evaporator tube to insure against corrosion, since the primary objective of the tests was to determine potential fouling due to organic contaminants. Any corrosion of the heat transfer surface would distort fouling observations.

The separator was simply an 8-inch section of 8-inch black iron pipe with a tangential inlet and topped with a 30-inch section of 5-inch pipe packed with Raschig rings. A 1-inch pipe was fitted to the bottom of the separator to drain underflow or blowdown. The purpose of the separator was twofold: First, it was a means of separating the vapors from the concentrated wastes so the concentrate could be measured and compared with the waste-water feed rate to establish evaporation rate, and second, it was to provide condensing and absorbing action by spraying water over the packing for odor control as required. It was never necessary to effect the second objective since no noticeable odors were given off with the vapors.

The waste-feed pump was a small "Moyno"-type pump fitted with a stainless steel rotor and oil-resistant rubber stator in a cast-iron body. After the first run, the pump was fitted with a split-pulley, variable-speed drive to control waste-water feed rate.

The steam generator was an Ebco electric steam boiler rated at 101,000 Btu per hr and 250 psig. The boiler was equipped with an ammeter, which was used for indicating steam output. With the exception of steam piping, all connections between equipment were by hose.

The Figures 3 and 4 show the details of the jacketed tube and separators, and the flow scheme used in the tests. After the first test, the vapor and concentrated waste-water discharge from the top of the evaporator tube was revised. The thermometer at the tube top was not giving correct readings. The side branch of the 1-inch stainless steel tube tee was closed with a length of hose whose end was blanked with a galvanized iron cap and nipple. A black iron tee was fitted to the top stainless steel-threaded adapter. The side branch of the tee was bushed down with a galvanized bushing and fitted with a nipple to receive the connecting hose and clamp. A brass thermowell was fitted to the top branch of the tee through a stainless steel bushing. The variable materials of construction were used so that corrosion could be observed after completion of the runs.

A spot sample of secondary effluent was collected on May 21 and titrated for observation of buffering effects that may be encountered in waste-water pretreatment during pH adjustment. Surprisingly no such effects were noted. The pH titration curve for this sample is shown in Figure 5. Analyses of composite samples of primary and secondary effluents that were used as feed during these tests are shown in Table 8.

The first test run was commenced on April 30, 1963. The effluent from the primary tanks was used as feed for the evaporator tube. The hose suction to the feed pump was fitted with a foot valve and dropped into the primary-effluent flume. No pretreatment of the waste water was attempted; it was fed to the evaporator tube as received in the flume. The waste-water feed pump was fitted with a v-belt drive with no provisions for varying the feed rate, which during this first run, was approximately 370 pounds per hour. The boiler steam pressure was 50 psig. The thermometer in the vapor-waste discharge tee at the top of the evaporator tube gave an erroneously low reading. When evaporation was visible, the temperature indicated was 205° F. After 4 days of operation the boiler amperage dropped and could not be restored by blowoff of noncondensables from the steam line. The top-tube temperature continued to drop and after 6 days of operation indicated 75° F. Severe tube fouling was obviously indicated. On the seventh day the unit was shut down and inspected.

Inspection of the tube showed a buildup of material about 1/8 inch thick throughout the tube. The material was not scale-like and was easily removed by passing a wire brush through the tube. When removed, the material was seen to be a gummy mass—an excellent thermal insulator. After removal of this overlying deposit, a thin film of scale material remained, which proved to be calcium carbonate.

There was no evidence of gummy material being baked on the tube. The heavy deposit was suspended matter that had adhered to the side of the tube. Calcium carbonate was of no concern in our evaluation of this run since we expected it to occur where no intrinsic treatment is available. When calcium carbonate deposition is a problem, it can be easily controlled by pH adjustment of the feed.

We concluded that primary effluent would require further clarification such as longer retention in settling tanks or filtration before it would be suitable for feed to a distillation system. In view of the limitations of the contract it was decided that

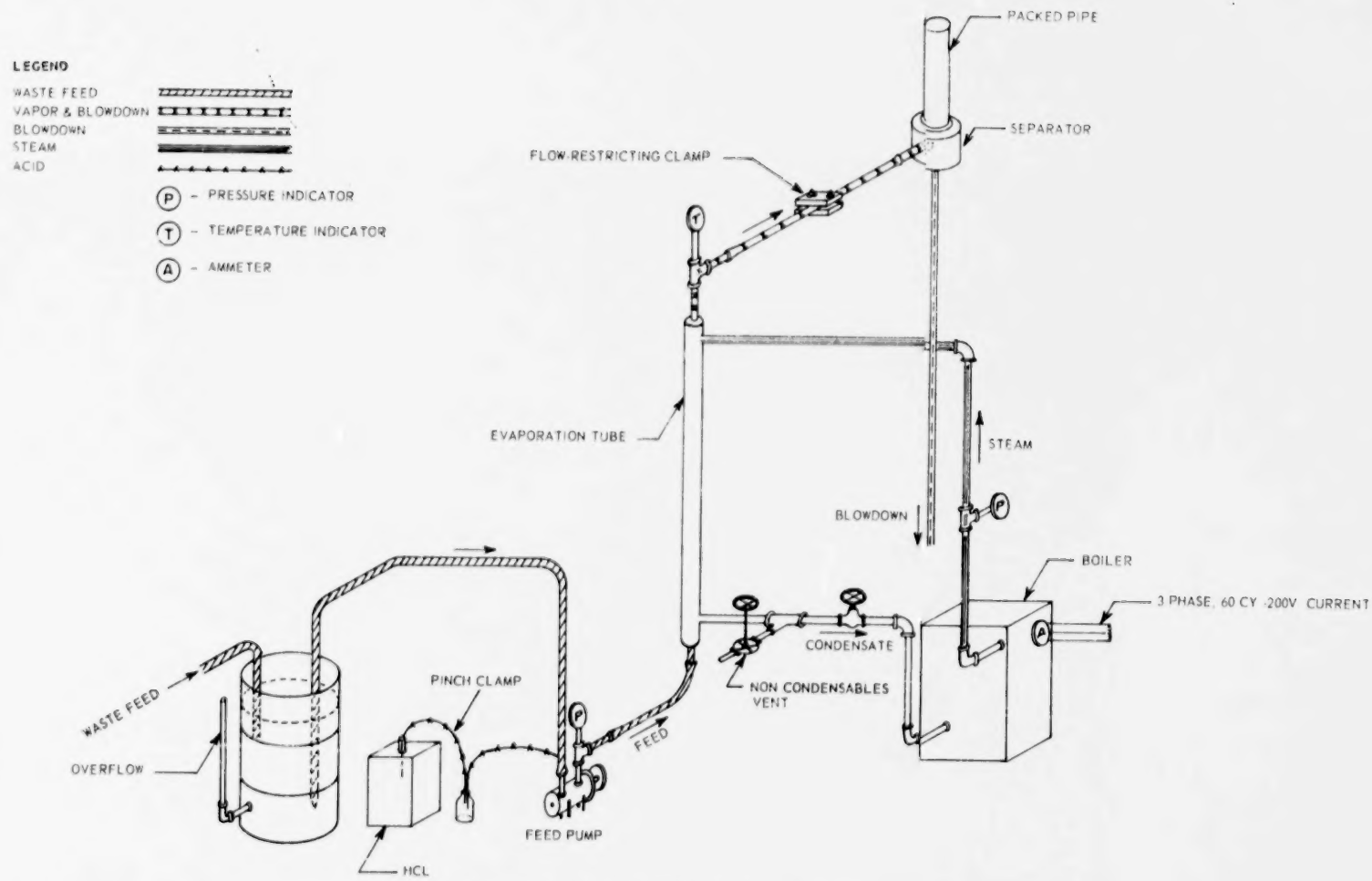

Figure 3. Tube-fouling test equipment.

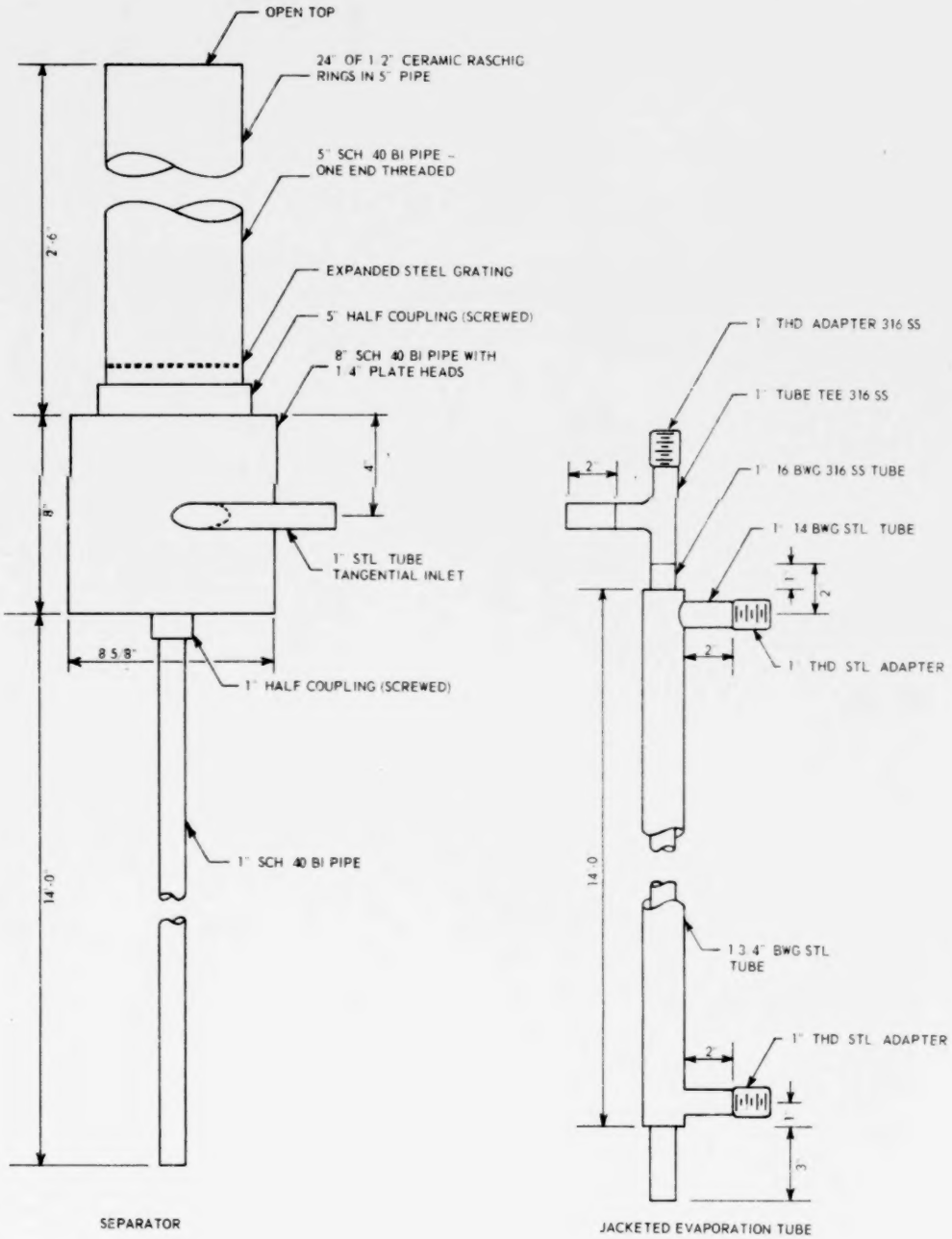

Figure 4. Evaporation tube and separator.

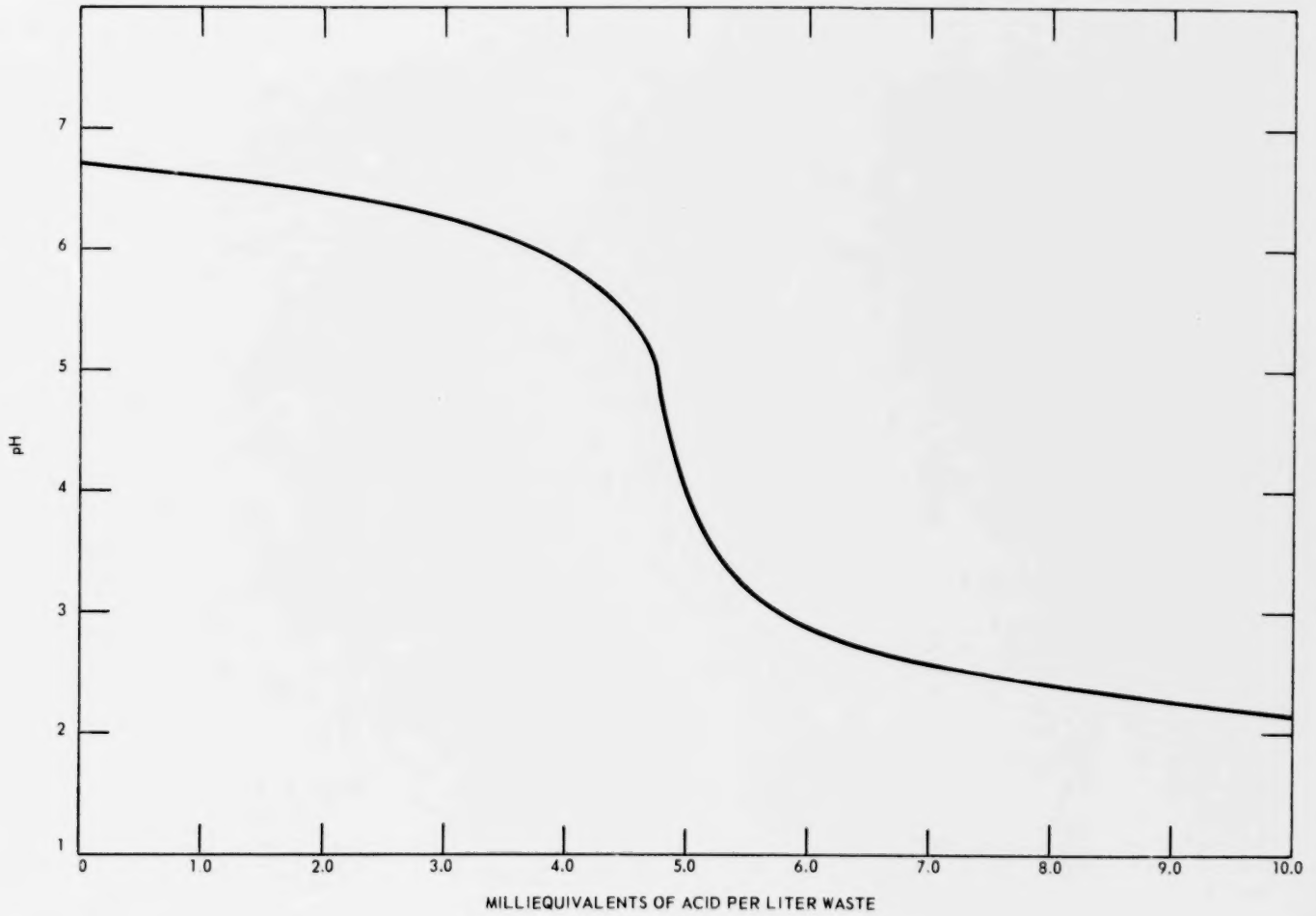

Figure 5. pH titration of Ann Arbor secondary effluent.

secondary effluent would be used for further tests so we would not have further difficulties with suspended matter.

The system was acid cleaned to remove calcium carbonate, the location of the thermowell was revised for a more accurate top-tube temperature reading, and a split-pulley variable drive was installed on the feed pump for control of waste-water feed rate.

Table 8. WASTE-WATER FEED ANALYSES

Constituent, ppm	Sample[a]			
	5-3	5-10	5-17	5-24
Ca^{++}	53	50	52	49
Mg^{++}	20	24	19	21
Na^{+}	130	60	62	80
K^{+}	25	13	15	17
NH_4^{+} (as N)	20	19	20	20
HCO_3^{-}	312	256	259	237
$SO_4^{=}$	82	85	110	115
Cl^{-}	75	69	89	96
NO_3^{-} (as N)	0.1	0.1	0.1	0.2
$PO_4^{\equiv}$ (Total)	15	16	19	24
SiO_2	12.7	11.0	10.8	11.0
pH	7.1	8.4	8.2	7.7
Hardness (as $CaCO_3$)	214	224	208	208
Alkalinity (as $CaCO_3$)	256	210	212	194
Conductivity, mmhos	1,150	820	830	960
Total dissolved solids	800	495	472	582
COD	224	76	65	77

[a] All samples were 7-day composites, collection commencing on May 3, May 10, May 17, and May 24 for primary-effluent sample 5-3, secondary-effluent sample 5-10, secondary-effluent sample 5-17, and secondary-effluent 5-24, respectively.

The second run used secondary effluent from the Ann Arbor Sewage Treatment Plant and was begun on May 8, 1963. After 2 days the boiler amperage (steamflow indication) dropped

and continued to do so to the end of the run, which lasted for 7 days, during which the average feed rate was 314 pounds per hour. The evaporation rate varied from a high of 15 percent to a low of zero, averaging about 4 percent for the run. The boiler pressure was 29 psig for this run. Evaporation was at atmospheric pressure (212° F).

The system was shut down on May 14 for inspection. Deposition was noted throughout the heat transfer area of the tube. With our limited ability to inspect the full length of the tube, we concluded that the deposition was uniform. It was cleaned with a wire brush followed by an acid rinse. The deposit collected by wire brush cleaning was treated with acid, and effervescence indicated a predominance of calcium carbonate. After effervescence subsided, a light material was observed floating on top of the acid. It was concluded that the deposit was calcium carbonate with a trace of occluded material.

The necessity for acid treatment of the waste for control of carbonate scale was evident, and for the next run an acid feed system, consisting of a carboy supply of inhibited 18° Baumé hydrochloric acid ("Duclean" No. 2), was included. Acid flow out of the carboy was controlled by a pinch clamp on rubber tubing. The acid dripped into a sealed bottle so the drop rate could be observed. Acid from the drop bottle was syphoned through a rubber tube into the pump hose suction through a hypodermic needle. The acid feed rate was, at best, difficult to control since the amount of acid required for carbonate neutralization was 1 drop every 6 seconds.

The third run was started on May 21 with acid feed and secondary effluent. The acid feed varied from a low of 1 drop every 24 seconds to a high of 1 drop every 2 seconds, averaging 1 drop every 4.7 seconds for the run. The steam pressure was 29 psig and evaporation temperature 212° F. The average feed rate for the run was 196 pounds per hour, and evaporation averaged 29 percent, varying from 5 to 56 percent. This run lasted for 8 days with no indication of tube fouling until the last day.

During the morning of the last day the acid feed dropped off and the blowdown pH was 7.2. The boiler amperage had dropped, indicating tube fouling. The acid feed was increased to bring the blowdown pH down to 5.3. Within 15 minutes the boiler amperage had been restored—a definite indication that the fouling resulted from calcium carbonate scale, which is easily removed by a reduction in pH. The unit was inspected on the afternoon of May 29. Just before inspection, a pH check showed the blowdown pH had again increased to 7.2. The acid feed was increased and

boiler amperage started to increase almost immediately. The unit was shut down for inspection about 20 minutes after the acid feed had been increased.

Inspection of the unit showed minor patches of scale material in the top or evaporating section of the tube. With the exception of these patches, the tube was clean and bright. It was concluded that this run showed that evaporation of waste water under these conditions is practical and that patches of scale noted resulted from carbonate deposition, which occurred under high pH conditions. The waste-water feed with adjusted pH had removed the majority of carbonate scale, and if the run had been continued for an additional half hour, probably no scale patches would have been observed. Hence, evaporation of secondary effluent without tube fouling appears entirely practical.

We were especially pleased with the absence of tube fouling at a high evaporation rate, and consequently at a high heat flux and wide temperature difference. From the second to the seventh day of this run, the evaporation rate varied from 20 to 56 percent averaging 39 percent, and the pH did not exceed 5.7.

When this run succeeded, we decided to try a fourth run at a higher evaporating temperature. A clamp was put on the discharge hose from the top of the evaporator tube to restrict the flow of vapor and blowdown and create a back pressure. This fourth run was begun on June 3, and lasted for 12 days. The patches of carbonate scale remaining from the third run were not removed for the fourth run. The boiler steam pressure was 39 psig, the evaporator feed rate averaged 229 pounds per hour, the pH averaged 5.2, and evaporation varied from 7 to 22 percent averaging 12 percent. The evaporation temperature fluctuated between 225 and 245°F averaging 234°F. The boiler amperage fluctuated, but did not establish a trend. Throughout the run there was no evidence of tube fouling, which would have affected evaporator performance.

The system was shut down on June 14 and inspected. The lower portion of the evaporator tube was clean and bright. A very thin film of light organic material was found in the top evaporation section of the tube. The film could be best described as what might remain after light-grade machine oil had been wiped over a metal surface. It was concluded that operation at higher evaporation temperatures was successful and that advanced waste treatment by distillation appeared practical.

From these tests we concluded that waste treatment by distillation will probably be applicable to renovation of waste water at temperatures equal to or exceeding those used for sea-water conversion, and that raw sewage, after removal of most of the suspended matter, may be used for distillation plant feed.

Observations for Corrosion

After the tube-fouling tests, the equipment was partially disassembled and visually inspected for corrosion. There was no attack on the stainless steel tube or stainless steel fittings. The 1-inch black iron tee that had been installed on top of the evaporator showed no evidence of corrosion. When it was removed, a light film of iron oxide covered its inside, but this can be attributed to exposure of the wet iron surface to the atmosphere.

A galvanized nipple and cap were used to block off the hose from the side branch of the stainless steel tee. This was a dead-end connection. No evidence of corrosion was noted.

The side branch of the 1-inch black iron tee at the top of the evaporator tube was fitted with a galvanized bushing and 3/4-inch nipple. The bushing showed some evidence of corrosion. The nipple showed severe, uniform, peripheral metal loss. One end was in the bushing, and a hose was clamped at the other end. When the nipple was removed from the bushing, only the threads remained. The metal loss at the other end (hose connection) was down to and, in one place, through the threads. There was no evidence of carbon dioxide, oxygen, or sulfide attack. (Sulfide attack is characterized by tuberculation with black deposition in the tubercule, oxygen attack, by pitting of the surface, and carbon dioxide attack, by etching or grooving of the surface.) Hence, we concluded that the uniform metal loss arose from low pH after acid pretreatment and high velocities. The brass thermowell was etched, which indicated ammonia attack on this copper alloy.

We would hesitate, however, to predict the extent of corrosion under plant operating conditions. Our observations were of fittings that had been a part of an evaporation system for a relatively short period—less than 2 months. In addition, the operation was neither closely controlled nor continuous. Longer operation under closely controlled conditions will be necessary before any valid conclusions can be drawn about the corrosion problems that may be encountered in advanced waste treatment by distillation.

Foaming Characteristics

Cursory observations were made of foaming characteristics of evaporating waste water during the tube-fouling tests.

1. Stable foam was observed during tube inspection in the top branch of the tee at the thermowell after the 2d, 3d, and 4th runs. Traces of this stable foam were also found in the side branch of the stainless steel tee when the blanking hose was removed after the last run. Both locations were dead spots with no circulation.

2. The foaming characteristics of the concentrated blowdown were observed by filling a bucket from a hose connection. The foam observed was no more nor less than that obtained by filling a bucket with secondary effluent in the same manner.

3. It was not possible to observe foaming inside the 8-inch pipe separator. Our only observation in this case was that foaming was not severe enough to build up through the Raschig ring packing of the 5-inch pipe atop the separator.

We conclude that foaming will occur in a waste-water evaporator system, but can probably be controlled by separators in the first stages of evaporation. Concentration of surface-active agents in the later stages of evaporation may become uncontrollable, and prefoaming may be required as a pretreatment step. Pilot studies for simulation of distillation operations through the last stages of evaporation will be required for final evaluation of foaming and its effect on advanced waste treatment operations.

Incremental Ion Increase

The data presented in Tables 1 through 5 were developed to predict the analyses of feed to distillation plants for the 22 reference cities.

The variation in incremental ion increase for the various references in Table 3 has a broad range. No attempt has been made to correlate ion increase with locale, tap water analyses, etc. We would, however, predict that the quality of municipal water will have some bearing on incremental ion increase and we would further predict that changing city water analyses through substitution of waste-water renovation for existing supplies will change the incremental ion increases.

Waste-water renovation by distillation, to be consistent with the goal of lowest possible water costs, will require a feed with the least possible pretreatment. We cannot visualize complete secondary treatment as a prerequisite to advanced waste treatment by distillation. Our evaluations have been based on ion increase through use plus secondary treatment. We should not expect a change in concentration of the majority of ions in raw waste water versus secondary effluent, but ammonia, nitrate, and phosphate concentrations, as well as the alkalinity, may be expected to change through sewage treatment.

The total cations and anions in the distillation feed analyses do not balance. This indicates inaccuracies, of course, but our evaluations are based on concentrations of particular ions and do not require a complete and accurate water analysis.

Closed-System and Parallel Operation

Evaluation of distillation in advanced waste treatment has been based on the assumptions that the concentration of each inorganic contaminant will be the sum of the ion concentration in the product water analyses and the ion increase through municipal use, and also that the quality of the product water delivered to the city water mains will be within the limits of the maximum "acceptable" concentrations, as in Table 6. These two assumptions dictate the parallel operation of a distillation plant and an adsorption plant, and closed-system operation with respect to processing of waste water and to product water use.

We shall first compare the average inorganic analyses of secondary effluent and of distillation feed in Tables 2 and 5, respectively. With the exception of the pretreatment required, either waste water could be handled equally well in a distillation plant. If distillation were to be used simply as a tertiary treatment, economic advantage would not be taken of potential savings in water procurement, water treatment, and secondary waste treatment That is, costs of distillation as a tertiary treatment would be added to existing water and secondary waste treatment costs, and in most cases would be prohibitive. If a closed waste treatment - water supply system is used, the additional costs for the treatment would be partially offset by reduction in costs of procurement, of water treatment, and of conventional secondary waste treatment.

Take the example of a municipality requiring water at an average rate of 20 mgd. Assume the average incremental ion increase is such that a 50-50 split can be made in the waste-water feed to the combination distillation-adsorption plant. Also, assume water procurement and treatment costs (exclusive of distribution) are 13 cents per 1,000 gallons and waste treatment costs are 10 cents per 1,000 gallons.[2]

We estimate total distillation cost for a 10 mgd multiple-effect plant to be 51 cents per 1,000 gallons including 1 cent per 1,000 gallons for acid pretreatment. Sukenik and Joyce[3] estimate adsorption cost of 6 to 8 cents per 1,000 gallons as a conservative figure. If we use 8 cents per 1,000 gallons for cost of adsorption treatment after secondary treatment, the total costs for the adsorption stream will be 18 cents per 1,000 gallons. With a 50-50 split, the total water cost for the municipality exclusive of water distribution and waste collection costs will be 35 cents per 1,000 gallons. If distillation-adsorption is applied as tertiary treatment, (i.e., without re-use of the final effluent) the extra distillation-adsorption operation after secondary treatment would cost 29 cents per 1,000 gallons, but to this must be added 23 cents per 1,000 gallons for existing operations (water procurement and treatment plus primary and secondary waste treatment), giving a total cost, exclusive of water distribution and waste collection costs, of 52 cents per 1,000 gallons. The total costs, exclusive of water distribution and waste collection costs, will be 52 and 35 cents per 1,000 gallons for tertiary treatment and closed-system operation respectively. Clearly, in the illustrated cases, operation as a closed system will have an economic advantage of 17 cents per 1,000 gallons.

Another consideration in the economics of closed-system operation versus tertiary treatment is the use of intrinsic treatment for scale control. As an example, consider intrinsic treatment of calcium by phosphate. As previously stated, we would expect the majority of plants operating as a closed system to contain sufficient phosphate for precipitation of calcium. In the secondary-effluent analyses of Table 2, note that none of the 22 plants has sufficient phosphate. We can, therefore, state without reservation that we would expect to incur higher pretreatment cost with tertiary treatment than with closed-system operation.

Parallel operation of a distillation-adsorption plant is dictated by economics. While neglecting any clarification required for the evaporator feed stream, a comparison of parallel distillation-adsorption operation with distillation alone shows that parallel operation has a 17-cent-per-1,000-gallons economic advantage (52 cents versus 35 cents per 1,000 gallons) in the previous example. In addition, distillate is unsuitable as such for a municipal water supply; it requires the addition of salts.

An interesting aspect of parallel operation in a closed system is the ability to vary the distillation-adsorption split (f) to minimize cost. It is conceivable that minimum cost of operation could occur at an (f) above the value required to achieve satisfactory product quality. If maximum operating temperature were significantly increased as (f) increased, because of a decreasing scaling tendency, such a situation would exist.

Comparison of Advanced Waste Treatment With Saline-Water Distillation

Two general differences are evident in a comparison of sea water with waste water. The first is that the inorganic composition of sea water is relatively constant as compared with waste water. A detailed investigation would probably show as many variations of inorganic composition as municipalities sampled. Second is that, although sea water contains both organic matter for the support of marine life and products of marine life, the

quantity of organics in sea water is insignificant when compared with municipal waste water. With the exception of controlling marine growths in auxiliary equipment, organic matter has no effect on operation of sea-water distillation plants.

The possible corrosion problems to be encountered in waste-water evaporation have been previously outlined. In comparison with sea-water corrosion problems wherein the major concern is handling of brine and removal of carbon dioxide and oxygen, pilot studies may show ammonia or sulfide attack on copper alloys to be the major problem in waste-water distillation. In this case a significant change in materials of construction may be dictated. Copper alloys are common materials of construction for heat exchanger tubes in sea-water distillation, but their use may not be possible in advanced waste treatment owing to ammonia or sulfide attack.

Intrinsic scale control in advanced waste treatment has also been outlined along with potential fouling due to organic contaminants. Sea water requires complete scale control for $CaSO_4$, $Mg(OH)_2$, and $CaCO_3$. Comparing this scale potential on the basis of ion product for sea water with that of average distillation feed for advanced waste treatment (Table 5), we obtain the following (Table 9).

Table 9. ION PRODUCTS OF SCALING MATERIALS

Scale	Sea water	Municipal waste water
$CaSO_4$, ppm^2	1.2×10^6	2.3×10^3
$Mg(OH)_2$, ppm^3	2.2×10^6	5.9×10^4
$CaCO_3$, ppm^2	6.0×10^4	8.4×10^3

It is evident that the comparative scale problems should be much less for the majority of waste treatment plants even without intrinsic scale control.

Three significant differences will exist between the equipment for sea-water conversion and that for water renovation plants in advanced waste treatment. We should expect to find volatile organic contaminants in the product water from waste-water evaporation. Equipment in addition to that required for sea-water conversion must be used to remove these contaminants. Removal might be carried out in the vapor phase. It might be carried out after condensing by supplementary treatment such as adsorption. A second difference is the method of providing a heat

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sink (required in all distillation operations except those based solely on thermocompression). Sea-water conversion plants use the ocean as a vast heat sink, but no such condition is found in inland cities. A well, lake, or river water supply must be available for a heat sink, or extra equipment such as a cooling tower must be provided.

Finally, sea water has a total dissolved solids of 36,000 ppm, while, on the basis of data available, it is rare for total dissolved solids in waste water to reach 2,000 ppm. Sea-water conversion fortunately does not require complete evaporation of the feed. Sea water is evaporated to the point where the increase in boiling-point rise makes further evaporation uneconomical. This is usually at a concentration factor of 2 to 4. Waste-water distillation on the other hand will require essentially complete evaporation or evaporation to the point where the waste constituents are concentrated enough for ultimate disposal, such as by incineration. Boiling-point rise in waste-water distillation will not be significant in any but the last evaporator effect. Sea water, on the other hand, has a range in boiling-point rise from slightly over $1^{\circ}F$, at initial concentration and $250^{\circ}F$, to $4.5^{\circ}F$, at a concentration factor of 4.5 and $130^{\circ}F$. The absence of reduction of boiling-point rise permits operation of an evaporator with a higher heat flux or lesser heat exchange area.

A background of information on sea-water conversion by evaporation is helpful in an evaluation of waste-water distillation. There is, however, a significant difference. Development of techniques for evaporation of sea water was evaluated in pilot studies. Distillation of waste water will also require pilot studies, and a program for development of design data will be necessary.

The Waste-Water Renovation Complex

A conception of equipment and facilities to be provided in a waste-water renovation plant is helpful in a comparison of waste-water distillation with sea-water conversion. The heart of the complex is the distillation equipment, which includes the basic evaporator with a thermocompressor and an auxiliary steam boiler or a steam boiler alone as a prime heat source.

An adsorption plant will be placed in parallel with the distillation equipment, which will probably be followed by a smaller "polishing" adsorption plant for removal of volatile organic contaminants.

The feed will be split between the distillation system and adsorption plant and reblended as final product water. An alternate to this method is operation of the distillation and adsorption plant in series. In this case the feed will be split, about half being fed to the distillation plant and the remainder being bypassed and reblended with the product distillate. The combined flow would then be fed to the adsorption plant, which would be designed for full-volume flow but with the same removal capacity for organic contaminants.

The distillation plant and adsorption plant will be designed or sized on the basis of average expected flow plus a safety factor. Flow rates from a municipal sewerage system may vary as much as 100 percent, depending upon the time of day, day of week, and season of the year. Economics will dictate maximum design capacity. The waste water must be impounded for about 2 to 4 days to insure a relatively constant feed supply to the advanced waste treatment plant.

During impoundment, advantage may be taken of separation, which will occur in the form of settling and flotation. The usual considerations such as drag line cleaning and skimming for removal of settled and buoyant matter must be provided. It may be necessary to control septic conditions during impoundment by aeration through sprays placed around the reservoir.

We would not expect to find a perfect balance between municipal water production and municipal waste-water flow. It may be necessary to provide additional water makeup to the system at times and provide for discharge of processed water to a receiving stream. This is a dual-purpose system; it takes the place of a sewage treatment plant and a municipal water treatment plant. As such, it must process all waste water received by it and supply the water demands of the municipality. Makeup to the system may be added to the plant feed or blended with the product water depending on makeup quality. The discharge of excess water from the system should be made as product water. That is, we should not lose sight of the objectives of advanced waste treatment. Waste water should not be discharged to a receiving stream unless its quality is as good as that of the receiving stream.

As previously noted, required pretreatment of waste water prior to distillation will vary with the incremental ion increase of the municipality served. Treatment of waste water between the impounding reservoir and distillation plant will vary from no treatment for waste water with intrinsic treatment, through acidification for carbonate scale control, to lime-soda ash treatment with acid backfeed. For the majority of cases considered, intrinsic

treatment through incremental increase of phosphate and silica is significant, and for the system under consideration, a chemical feed system for supplemental phosphate and silica or an acid feed for pH control will suffice.

A distillation plant will not have 100 percent thermal efficiency. We must, therefore, provide a heat sink in the form of cooling water for the final condenser. Water from wells, lakes, or rivers, if near the plant site, is the most economical source of cooling water. If this is not practical, a cooling tower using waste water for makeup is the next least costly operation.

Chlorination equipment as presently incorporated in municipal water treatment facilities will be required for chlorine feed to maintain a residual of free available chlorine in the final product water.

The last stage of the waste-water renovation complex is product water storage. There should be no reason why existing product water storage facilities, where peak flow demands are met, will not suffice.

Distillation plant outages should not be a problem, because of the storage provided and because of flywheel effect. That is, the plant could be off the line for some time, while total water supplies are handled by the adsorption plant only, before increases of inorganic contaminants would raise the concentration to intolerable limits.

In summary, waste water will enter the impoundment reservoir of the complex, which may act as a pseudo-primary treatment plant, possibly with facilities for aeration as required to control septic action. The liquid from the impounding reservoir will be split and be fed to the distillation and adsorption plants. To the feed to the distillation plant, phosphate and silica or acid will be added, based on the inorganic analysis of the waste-water feed. The product from the distillation plant will pass through a polishing adsorption unit and be reblended with the primary adsorption plant product water and delivered finally to the municipal water storage system. The required auxiliary equipment to provide cooling water to the final condenser will complete the complex.

Costs of Waste-Water Renovation

Much has been written about capital costs for sea-water conversion plants and associated operating costs for producing potable water — most of it controversial. It is difficult to find agreement on capital cost requirements for the same type plant at various capacities even when the costs are presented to demonstrate reduction in capital expenditure per unit product with increasing capacities. When costs are developed to compare various methods of sea-water distillation, the picture becomes even more distorted. An examination of the literature shows cost figures for existing, operating, demonstration plants that have been revised, adjusted, and extrapolated to the point where there is no resemblance to proved operating costs and capital expenditure.

The first step in developing costs for waste-water distillation is establishment of base costs for sea-water conversion plants and adaptation of these costs to waste-water renovation. Adjustment should be made for pretreatment costs where required, costs associated with addition or deletion of equipment, costs of construction materials, etc., of which all are either variable with respect to the municipality to be served or are yet to be defined in future pilot plant studies. It is obvious that presentation of estimated costs for waste-water distillation must be made with qualification.

The two distillation methods that currently show the lowest capital and operating costs on sea water are multi-stage flash (MSF) and multiple-effect, long-tube vertical (LTV). One-million-gallon-per-day plants to demonstrate these methods have been built at Freeport, Texas (LTV), and San Diego, California (MSF), under the Demonstration Plant Program of the Office of Saline Water. Capital and operating costs of these two relatively small plants are quite similar. Only the LTV system will be considered in an estimation of advanced waste treatment costs for the following reasons.

1. Having prepared quotations on LTV plants with capacities of 0.5 to 15 mgd, we are more sure of the accuracy of cost estimates for LTV plants and of the conversion of these costs to operation for advanced waste treatment.

2. A multiple-effect plant can concentrate the waste to almost any desired density with very little penalty in cost. Only a small proportion of the water is evaporated in one pass from high to low temperature in a flash plant. If, therefore, a high recovery of product water is required as in advanced waste treatment, either a number of flash systems must be compounded or else the entire system must operate at essentially the final discharge concentration.

3. A multiple-effect system is more amenable to incorporation of thermocompression for further improvement in economy.

Estimates of capital and operating costs of LTV plants on sea water are shown in Figures 6 and 7 for capacities from 1 to 17 mgd of fresh water. These estimates are based on the following conditions.

1. Maximum sea-water temperature limited to 250°F to avoid calcium sulfate scaling;

2. de-aeration and decarbonation with sulfuric acid to avoid corrosion and scaling;

3. copper alloy (admiralty metal) heating surfaces throughout; steel piping and vessels when in contact with de-aerated sea water;

4. steam supplied from on-site, high-pressure boiler fired with gas or oil;

5. steam turbine and generator included to provide power for all pumps, which would be motor driven, with the exhaust from the turbine providing part or all of the heat for the evaporator.

The capital costs of Figure 6 include everything from steam generation to sea-water intake, buildings for offices and shops, initial supplies, and plant startup. They do not include the cost of land or working capital. The costs of two types of LTV plant are shown. The first is a straight 14-effect evaporator. This plant would use so much steam relative to power consumption for pumps that a boiler pressure only moderately higher than the evaporator steam pressure would be needed for power generation. A boiler for appreciably higher pressures is not much more expensive per unit of capacity. This permits generation of additional power, which can be used to drive a vapor compressor of a thermocompression

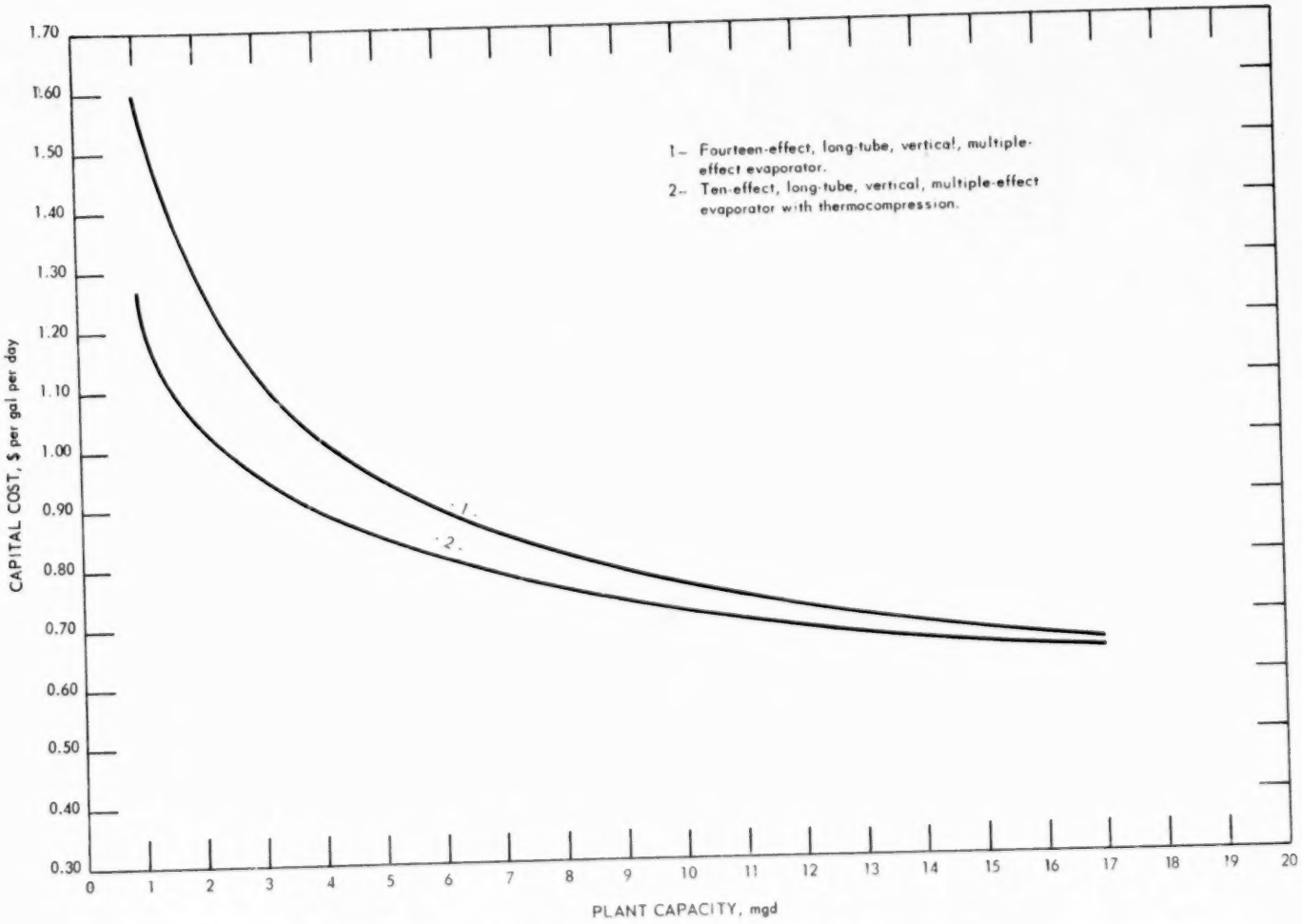

Figure 6. Capital costs of sea-water conversion plants.

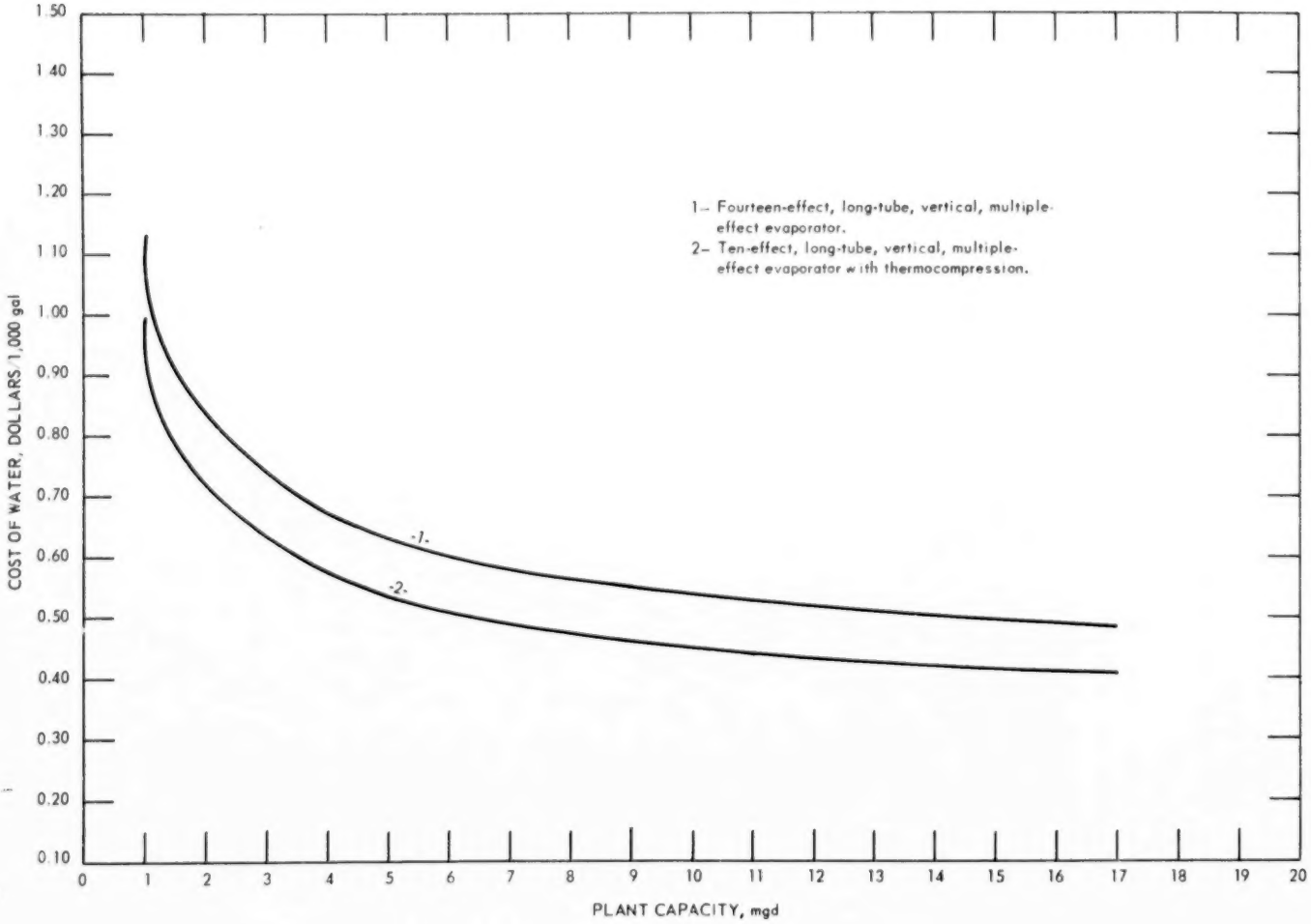

Figure 7. Operating costs of sea-water conversion plants.

evaporator. The costs of this type of plant are shown in the second curve of Figure 6, based on the assumption that the multiple-effect section of the plant would have 10 effects. Capital costs of this combination-type plant are somewhat lower than those of the 14-effect plant, because the plant is more efficient, requiring a smaller boiler capacity, and because an appreciable part of the total evaporation is accomplished in the thermocompression section at high temperatures, where heat transfer coefficients are much higher, and heating surface requirements lower.

The cost of water from these plants, for distillation of sea water, is shown in Figure 7. A breakdown of the annual operating costs for 10 mgd plants is shown in Table 10.

Table 10. OPERATING COSTS OF DESALINATION PLANTS (ANNUAL PRODUCTION – 10 mgd for 330 days per year)

Type plant	Multiple effect	Thermocompression-multiple effect
Amortization at 7.4%	$ 556,000	$ 529,000
Maintenance, material, and labor at 2.6%	$ 195,000	$ 186,000
Fuel at 30¢/10^6 Btu	$ 832,000	$ 576,000
Operating and supervisory labor	$ 135,000	$ 135,000
Supplies	$ 50,000	$ 50,000
TOTAL	$1,768,000	$1,496,000
Cost of distilled water, ¢/1,000 gal	53.6	45.3

If plants such as these were built for advanced waste treatment instead of for sea-water conversion, the capital and operating costs would be somewhat lower, for the following reasons.

1. Since more water would be distilled from the feed, less feed would be required per gallon of product water. This would save on heating surface and on heat required for feed preheating, and less pumping power would be required.

2. Since advanced waste treatment feed has a low initial-solids content most of the evaporation could be accomplished under conditions such that there would be no loss due to boiling-point elevation. This would represent a saving of 18 to 19 percent of heating-surface requirements relative to those of sea-water conversion.

3. Since advanced waste treatment feeds can be treated for scale prevention, the upper operating temperature is no longer limited to 250°F, which permits more evaporation per unit of heating surface.

An advanced waste treatment plant may require additional equipment, and for the sake of comparison with sea-water conversion, we can assume requirements for chemical pretreatment, cooling tower, and adsorption polishing. If it is assumed that an advanced waste treatment plant is limited to 250°F as an upper operating temperature and that all but 0.2 percent of the waste water is recovered as distilled water (the last few percent being recovered in a forced-circulation evaporator effect heated by vapor bled from the main LTV evaporator), the savings shown in Table 11 should be possible.

Table 11. WASTE-WATER DISTILLATION COSTS FOR TOP TEMPERATURE OF 250°F

Item	% less than for sea-water conversion
Capital cost	15
Fuel cost	1.4
Product water cost	7.1

If it is assumed that the plant can be built for operation at 350 instead of 250°F, the potential cost reductions are even more impressive. If it is assumed that the number of effects used is increased in proportion to the total available temperature difference, the savings shown in Table 12 are possible.

Table 12. WASTE-WATER DISTILLATION COSTS FOR TOP TEMPERATURE OF 350°F

Item	% less than for sea-water conversion
Capital cost	27
Fuel cost	13
Product water cost	19

These estimates take into account the effect of the higher pressures involved in 350°F operation, which proves to be insignificant. At the higher pressures, heat transfer coefficients are improved and so smaller steam chests are required. Vapor volumes are also lower, resulting in smaller vapor-liquid separators. In addition, only a small part of the evaporation takes place at pressures higher than a vessel could withstand if designed only for the full vacuum conditions encountered at startup and shutdown.

One further advantage is possible if waste-water evaporation can be accomplished at higher temperatures than is currently possible with sea water. The upper limit of size of a thermocompression-multiple effect sea-water plant is fixed by the size of reasonably priced vapor compressors. As operating pressures and vapor densities increase, the capacity of available compressors increases, making it possible to build larger single-unit plants. For a 350°F top temperature, the single-unit plant capacity would increase from about 17 to 90 mgd, with a consequent further reduction in costs.

The over-all cost of waste-water renovation is of ultimate importance; and so distillation costs must be adjusted on the basis of that portion of the total waste (f) that will be fed to the distillation plant, and to this must be added the cost for adsorption to establish the final product water cost. The variation of (f) is from 23.6 to 63.7 percent- too extensive to establish an expected value that would be applicable to the majority of cases. We have, however, presented enough data for examination of a specific case.

We have considered a maximum operating temperature of 400°F in this report. Although selection of 400°F was somewhat arbitrary, it was influenced by consideration of design pressure and calcium sulfate solubility data. The economics of higher temperature operation will, at some point, be offset by increased costs for higher pressure equipment fabrication and pumping requirements. At 400°F a penalty of 2.8 psi increase in operating pressure is imposed for each degree F increase in temperature. Also, at 400°F, calcium sulfate solubility data are sketchy and further assumptions as to maximum permissible temperature without calcium sulfate scale deposition are dangerous.

Apparently, 400°F operation will be above the economic operating temperature for some systems. Assumptions were made and a simplified formula for operating costs of a multistage flash (MSF) system was developed that considered only recycle pumping and steam costs. This was used to optimize MSF operation for various temperature increases through the steam

heater. A plot of the optimum operating temperature versus steam/power cost ratio is presented in Figure 8 to illustrate the existence of a maximum operating temperature. An attempt was made to apply the same principles to LTV operation, but a simplified cost formula could not be developed.

A study of MSF maximum operating temperature, made by the University of California,[4] concluded that the maximum economic operating temperature lies between 350 and 400°F. The variables or factors influencing the maximum economic temperature considered in this investigation were extensive.

Recommendations for Future Work

Evaluation of the applicability of sea-water conversion plants for supplying potable water for a given area requires consideration of capital costs with amortization and interest on investment, operating labor costs, maintenance, chemical costs, and steam and power costs. A balance is achieved among these costs to give the lowest over-all cost per unit quantity of water produced for a particular case. Variations of these costs dictate individual evaluations for each proposed installation, and this applies also to waste-water renovation plants. A major difference in making such evaluations is the composition of feed to the distillation plants. The composition of sea water is relatively constant, but the variations in composition of waste-water feed are practically infinite, and these variations make individual evaluation even more critical.

As an intermediate step towards complete evaluation of an individual installation we must examine in greater detail the corrosion and fouling problems associated with waste-water distillation, the effectiveness of various treatment methods in controlling these problems, the mechanical operations such as defoaming or filtration for preconditioning wastes prior to distillation, the materials of construction under simulated operating conditions, the effect of volatile organic contaminants in the vapor phase between evaporation stages, and the polishing techniques necessary to remove volatile organic contaminants from product water.

To this end we recommend that studies be made on a pilot plant scale. The pilot plant should be provided with equipment sufficient to operate three stages of an evaporator, preconcentration equipment to simulate all stages of evaporation from 400 to 90°F, waste-water-preheating equipment, and condensers. Provisions should be made for pretreating wastes by defoaming,

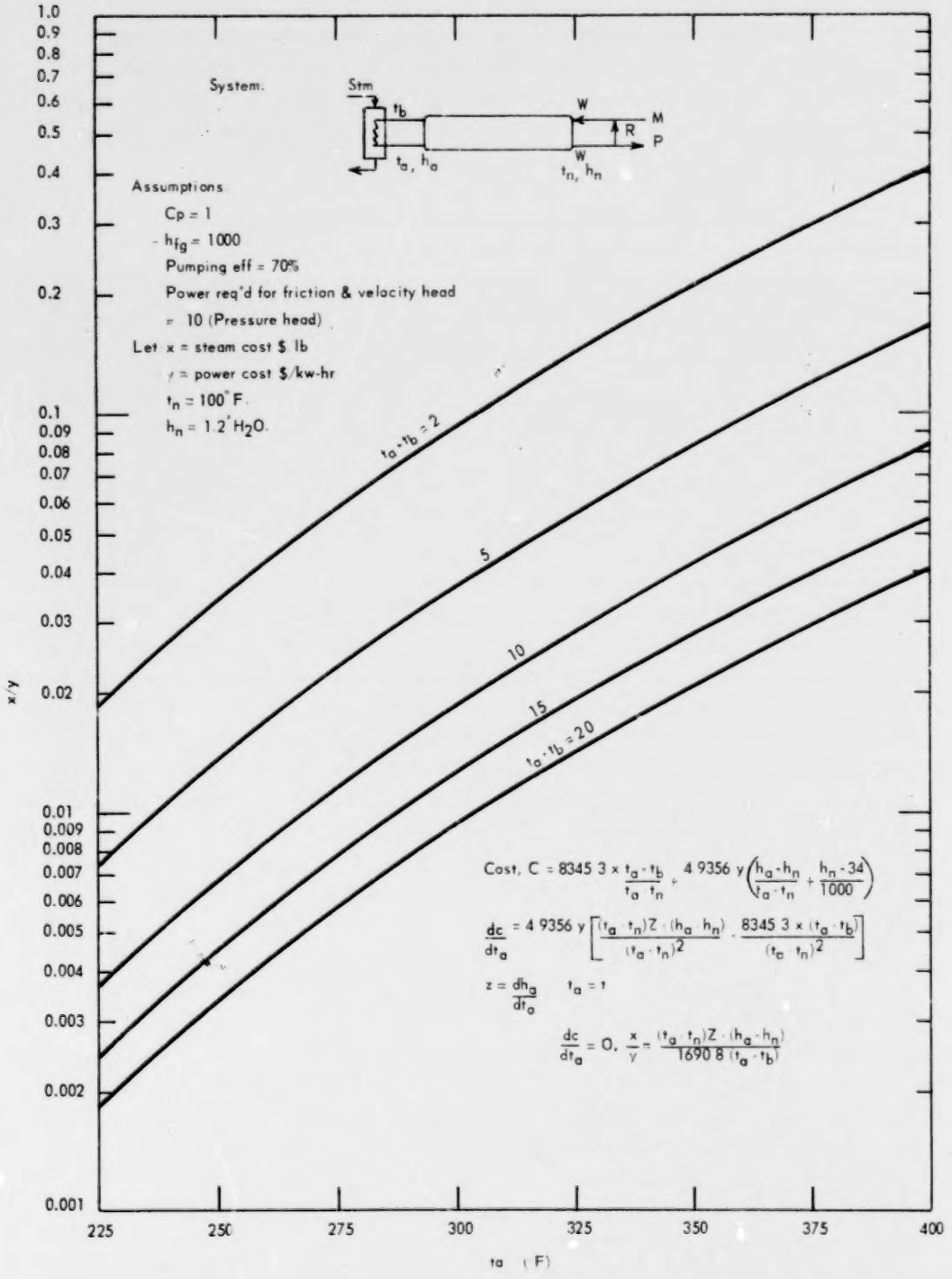

Figure 8. Maximum economic operating temperatures for MSF.

settling, filtering, softening, and by adding conditioning chemicals. Aside from various materials of construction used in heat exchanger tubes, test spools should be located throughout the system for more complete definition of corrosion rates and mechanisms. The evaporators should be so constructed as to facilitate removal of tubes for inspection and for changes in materials of construction.

Our studies have shown that on the basis of the inorganic contaminants to be expected, 400°F operation of distillation equipment is practical. The equipment should be so designed that studies relative to decomposition and degree of volatilization of organic contaminants can be made under all anticipated operating temperatures.

In the initial stages of pilot plant work every attempt should be made to use raw sewage for distillation feed and with a minimum of pretreatment.

Studies conducted under this contract indicate that evaporation for waste-water renovation is practical and that the program should be continued to obtain background data so this process can be completely evaluated for any particular application. The need for this type of waste-water renovation in areas of the United States is urgent.

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